U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-292 709

Kinetics of Sulfur Dioxide in Aqueous Solution

Illinois Univ, Urbana

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, NC

Jan 79

PB 292709

United States
Environmental Protection
Agency

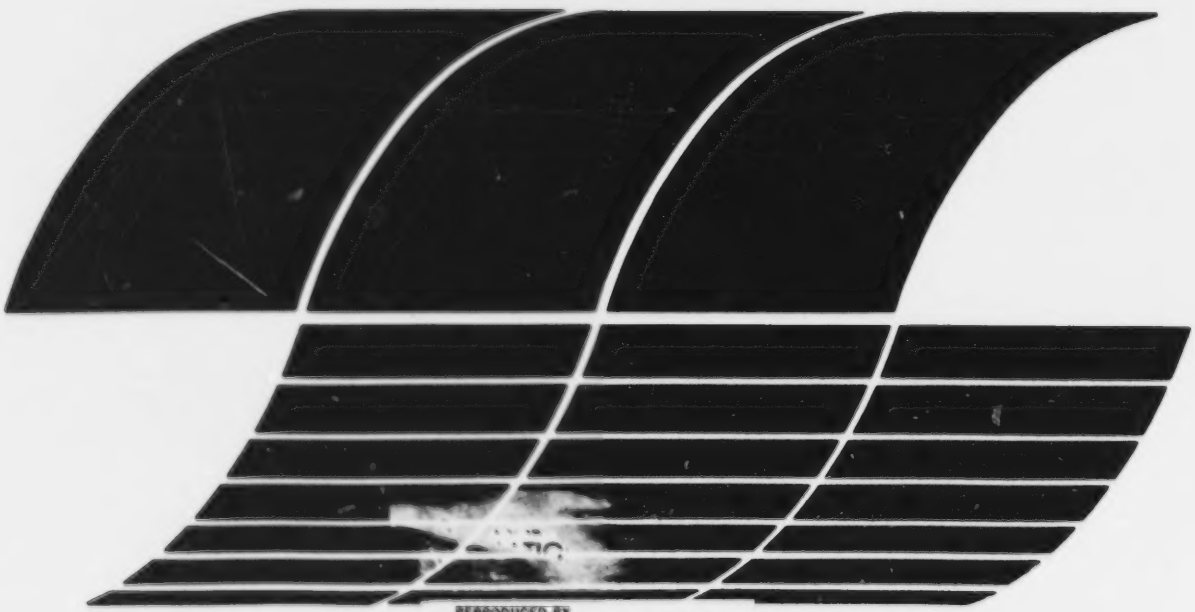
Industrial Environmental Research
Laboratory
Research Triangle Park NC 27711

EPA-600/7-79-030
January 1979

EPA

Kinetics of Sulfur Dioxide Oxidation in Aqueous Solution

Interagency Energy/Environment R&D Program Report



REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the INTERAGENCY ENERGY-ENVIRONMENT RESEARCH AND DEVELOPMENT series. Reports in this series result from the effort funded under the 17-agency Federal Energy/Environment Research and Development Program. These studies relate to EPA's mission to protect the public health and welfare from adverse effects of pollutants associated with energy systems. The goal of the Program is to assure the rapid development of domestic energy supplies in an environmentally-compatible manner by providing the necessary environmental data and control technology. Investigations include analyses of the transport of energy-related pollutants and their health and ecological effects; assessments of, and development of, control technologies for energy systems; and integrated assessments of a wide range of energy-related environmental issues.

EPA REVIEW NOTICE

This report has been reviewed by the participating Federal Agencies, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Government, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This document is available to the public through the National Technical Information Service, Springfield, Virginia 22161.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-79-030	2.	3. RECIPIENT'S ACCESSION NO. PB292709
4. TITLE AND SUBTITLE Kinetics of Sulfur Dioxide Oxidation in Aqueous Solution		5. REPORT DATE January 1979 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) J. L. Hudson, J. Erwin, and N. M. Catipovic		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS The University of Illinois Urbana, Illinois 61801		10. PROGRAM ELEMENT NO. EHE624 11. CONTRACT/GRANT NO. Grant R800303
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 4/73 - 12/74 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Norman Kaplan, MD-61, 919/541-2556.

16. ABSTRACT The report gives results of a study of the rate of oxidation (low pH catalyzed oxidation and high pH uncatalyzed oxidation) of SO2 in a 1 liter semi-batch reactor. Low pH experiment results included: (1) both MgSO4- and MnSO4-catalyzed liquid-phase oxidation of SO2 at low pH are zero order in SO2 concentration; (2) while Mn is a very effective catalyst even at concentrations as low as 3 ppm, Mg shows little catalytic action even at concentrations as high as 20,000 ppm; (3) energy of activation for the Mn-catalyzed reaction was 18.7 kcal/mole; (4) low pH oxidation of SO2, catalyzed by MnSO4, is independent of pH between 1 and 4, while at pH values above 4, the reaction speeds up due to the presence of sulfite ions; (5) ionic strength did not appear to affect the reaction rate significantly (additional tests at higher ionic strengths should be performed to check this effect); and (6) sulfate ions inhibit the reaction significantly. The primary result of the high pH study was a first order rate constant of 0.0053 per second; during the experiments, oxidation was kinetically controlled with a constant oxidation concentration of 0.0013 M. Results applied to conditions in a SO2 scrubber indicated that the catalyst effect, even at ppm concentration, is very significant. The effect of catalysts in high pH scrubbing systems subject to oxidation is much greater than in low pH systems.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Sulfur Dioxide	Stationary Sources	07B
Oxidation		07C
Kinetics		20K
Catalysis		07D
Manganese		
Magnesium		

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 82
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE PC A05/MF A01

EPA Form 2220-1 (9-73)

EPA-600/7-79-030

January 1979

Kinetics of Sulfur Dioxide Oxidation in Aqueous Solution

by

J.L. Hudson, J. Erwin, and N.M. Catipovic

The University of Illinois
Urbana, Illinois 61801

Grant No. R800303
Program Element No. EHE624

EPA Project Officer: Norman Kaplan

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, DC 20460

ABSTRACT

The rate of oxidation of sulfur dioxide was studied in a one liter semi-batch reactor. There were two aspects of the study, viz., low pH catalyzed oxidation and high pH uncatalyzed oxidation.

The results of the low pH experiments were as follows. Both $MgSO_4$ and $MnSO_4$ catalyzed liquid-phase oxidation of SO_2 at low pH are zero order in SC_2 concentration. While manganese is a very effective catalyst even at concentration as low as 3 p.p.m., magnesium shows little catalytic action at concentrations as high as 20,000 p.p.m. Energy of activation for the Mn-catalyzed reaction was found to be 18.7 kcal/mole. Low pH oxidation of SO_2, catalyzed by $MnSO_4$, is independent of pH between 1 and 4, while at pH values above 4 the reaction speeds up due to the presence of sulfite ions. Ionic strength did not appear to affect the reaction rate significantly, but additional experiments at higher ionic strengths should be performed to check this effect. Sulfate ions inhibit the reaction significantly. Kinetic results can be presented conveniently using the ratio $(SO_4^=)_{added}$ to $(S\Phi_2)$ initial. The mechanism of the reaction seems to involve complexing of Mn with $SO_4^=$, but further work is necessary to make definite conclusions.

The primary study of the high pH case was a first order rate constant of 0.0053 sec^{-1}. The experiments were carried out under conditions such that, the oxidation was kinetically controlled with a constant oxygen concentration of 0.0013 M.

Finally the results were applied to conditions in a sulfur dioxide scrubber. The catalyst effect even at p.p.m. concentraion is very significant. The effect of catalysts in high pH scrubbing systems subject to oxidation is much greater than in low pH systems.

Studies carried out with chelating agents showed that previously studied "uncatalyzed" reactions were in fact primarily trace metal catalyzed.

CONTENTS

Abstract ii

Figures iv

Tables vi

I. Introduction 1

II. Previous Kinetic Work on Liquid-Phase Oxidation of Sulfur Dioxide 4

III. Low pH Catalyzed Oxidation of Sulfur Dioxide. 10

IV. High Ph Uncatalyzed Oxidation of Sulfur Dioxide 43

V. Uncatalyzed Studies 59

VI. Application of Kinetic Data on Sulfur Dioxide Oxidation to Scrubbers 61

VII. Further Studies 65

References 67

Appendix A 70

Appendix B 71

Appendix C 73

FIGURES

Number		Page
1	Effect of pH on the relative concentrations of SO_2 species in solution	2
2	Experimental apparatus.	11
3	SO_2 concentration as a function of time, with 20,000 p.p.m. $MgSO_4$ catalyst	16
4	SO_2 concentration as a function of time, with 1 p.p.m. $MnSO_4$ catalyst	17
5	SO_2 concentration as a function of time, with 3 p.p.m. $MnSO_4$ catalyst	18
6	SO_2 concentration as a function of time, with 1 p.p.m. $MnSO_4$ catalyst and lower $(SO_2)_{initial}$	19
7	Zero-order reaction rate constant, k_o, as a function of the initial pH, with 1 p.p.m. $MnSO_4$ catalyst	21
8	Zero-order reaction rate constant k_o, as a function of the initial pH, with 3 p.p.m. $MnSO_4$ catalyst	21
9	SO_2 concentration as a function of time, with 1 p.p.m. $MnSO_4$ and $pH_{initial}$ of 3.4	24
10	Zero-order reaction rate constant, k_o, as a function of $(SO_4^=)_{added}/(SO_2)_{initial}$ from Johnstone & Coughanowr's[24] data.	28
11	Zero-order reaction rate constant, k_o, as a function of $(SO_4^=)_{added}/(SO_2)_{initial}$, with 1 p.p.m. $MnSO_4$ catalyst.	29
12	Zero-order reaction rate constant, k_o, as a function of $(SO_4^=)_{added}/(SO_2)_{initial}$, with 3 p.p.m. $MnSO_4$ catalyst	30
13	SO_2 concentration as a function of time, with 1 p.p.m. $MnSO_4$ catalyst and $(SO_4^=)_{added}/(SO_2)_{initial} = 1$.	31

Number		Page
14	SO_2 concentration as a function of time, with 3 p.p.m. $MnSO_4$ catalyst and $(SO_4^{=})_{added}/(SO_2)_{initial}$ = 10.	32
15	Dimensionless diagram of k_o(with sulfate added)/k_o (without any sulfate added) as a function of $(SO_4^{=})_{added}/(SO_2)_{initial}$ . . .	38
16	Effect of the "internally produced" sulfate	39
17	Reactor for high pH uncatalyzed oxidation of sulfur dioxide. . .	46
18	Rate of mass transfer of oxygen to solution containing 1.2×10^{-4} M $CoSO_4$ catalyst	50
19	Complete kinetic data for the uncatalyzed sulfite oxidation at a constant pH of 11.1	51
20	Average kinetic data dna standard deviations for the uncatalyzed reaction at a constant pH of 11.1	54
21	Natural logarithm of sulfite concentration as a function of time for the uncatalyzed reaction at a constant pH of 11.1	55
22	Complete kinetic data for the uncatalyzed sulfite oxidation at variable pH	56

TABLES

Number		Page
1	Results of kinetic experiments at various pH values	22
2	Results of Johnstone and Coughanowr[24]	27
3	Zero-order reaction rate constants for different experimental conditions	33
4	Results of kinetic experiments dealing with sulfate effects . . .	34
5	Ratios of k_o (with sulfate added)/k_o (without sulfate added) for various experimental conditions.	36
6	Kinetic results for the uncatalyzed sulfite oxidation at a constant pH of 11.1 (with average values and standard deviations).	52
7	Kinetic results for the uncatalyzed sulfite oxidation at variable pH	57

I. INTRODUCTION

The emission of sulfur oxides from stationary sources has become one of the most serious air pollution problems in the world. Sulfur dioxide is one of the major pollutants, formed mostly as a result of combustion of coal and oil with high sulfur content in power plants and industrial installations.

The liquid-phase oxidation of SO_2 is a very important factor in the air pollution problems caused by this gas. In aqueous solutions, sulfur dioxide readily undergoes oxidation to sulfate, especially in the presence of metal ions as catalysts. Formation of sulfate in SO_2 scrubbing systems has become one of the most important unsolved problems in the removal of SO_2 from stack gases by wet scrubbing. The oxidation of SO_2 in fog droplets in heavily polluted air has been partly responsible for some of the air pollution disasters in the past. This oxidation can also take place in cloud and rain droplets in relatively unpolluted atmospheres.

When sulfur dioxide comes into contact with water the product is hydrated sulfur dioxide, which can undergo dissociation to bisulfite or sulfite:

$$SO_2 \cdot H_2O \underset{k_{-2}}{\overset{k_1}{\rightleftharpoons}} H^+ + HSO_3^- , \qquad K_1 = \frac{k_1}{k_{-1}} \tag{1}$$

$$HSO_3^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H^+ + SO_3^{=} , \qquad K_2 = \frac{k_2}{k_{-2}} \tag{2}$$

The equilibrium constants for the dissociations have been the subject of a great deal of investigation, as reported by Powell[39]. In our work, we adopt the values $K_1 = 1.74 \times 10^{-2}$ (Tartar and Garretson[48]; Frydaman, Torsten and Sillen[15]) and $K_2 = 6.24 \times 10^{-8}$ (Yui[57]).

The relative concentrations of the bisulfite and sulfite ions depend greatly on the pH of the aqueous solution. Fig. 1 shows the effect pH on the relative concentrations of hydrated sulfur dioxide, bisulfite and sulfite. Although Fig. 1 may not be quantitatively exact because all activity coefficients are assumed to be unity, it does give a good qualitative idea of the relation between various SO_2 species and pH.

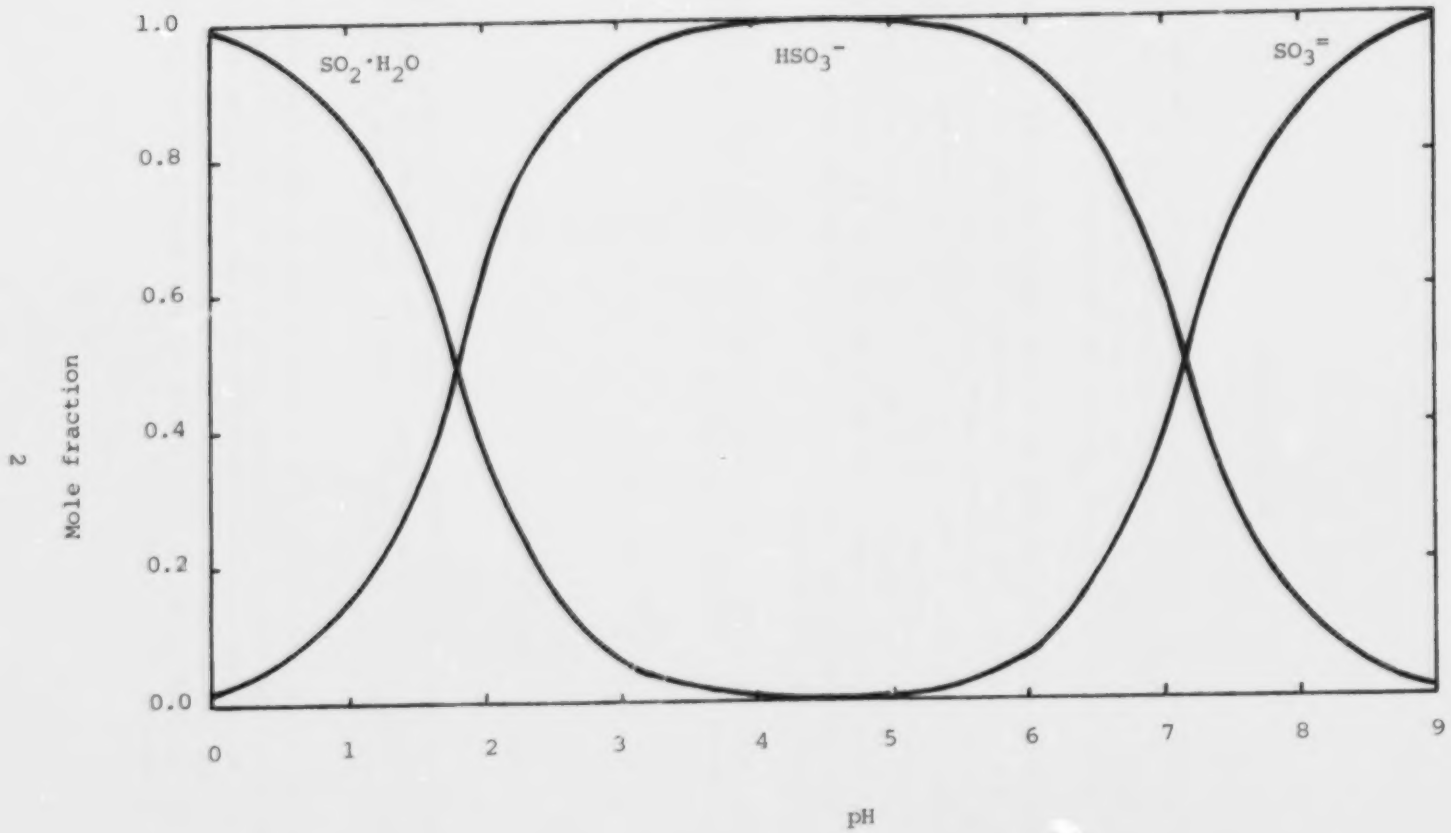


Fig. 1. Effect of pH on the relative concentrations of SO_2 species in solution.

When the oxidation of sulfur dioxide in aqueous solutions is discussed, it must be pointed out that the various species in solution react with oxygen at different rates. The oxidation of sulfite is the fastest process. Therefore, it is very important to know whether high pH or low pH oxidation is taking place. Also, various catalysts can greatly affect the oxidation rate; hence, it is necessary to differentiate between uncatalyzed and catalyzed SO_2 oxidation.

In industrial SO_2 scrubbers, sulfur dioxide is absorbed in the scrubbing liquid, the pH of which depends on the particular system used. The pH range can extend from 4 to 10. Various metal catalysts are inevitably present in the scrubbers. Sulfates formed by SO_2 oxidation must be either regenerated and removed from the system as solids or purged from the system in liquid form. In either case, additional scrubbing solution must be added to the system as make-up, and this significantly increases the operating cost of the process. Also, since the sulfate form of a salt is much more difficult to regenerate than the bisulfite or sulfite form, oxidation essentially represents a loss of SO_2 product in processes which involve regeneration of the absorbed SO_2. To be economically acceptable, regenerative scrubbing processes must minimuze this sulfate formation. SO_2 oxidation rates in scrubbers can reach values as high as 20-30% (% of total SO_2 absorbed which is oxidized) in some processes (for example, in the double alkali process which uses dilute sodium sulfite as the scrubbing solution).

In the atmosphere, SO_2 is absorbed by fog or rain drops and oxidized to sulfate, which is more toxic than the sulfur dioxide gas. Atmospheric oxidation can take place with the aid of metal catalysts which serve as condensation nuclei for water vapor or in the presence of ammonia when even the uncatalyzed reaction can produce significant levels of SO_4 due to the maintaining of a higher pH by NH_3.

The SO_2 liquid-phase oxidation process itself is poorly understood in terms of its kinetic characteristics and mechanism. Some studies that have been done have given contradictory results. The purpose of our study, therefore, was to perform kinetic experiments which shed more light on the factors that influence SO_2 oxidation. Since traces of metal salts that catalyze SO_2 oxidation are present in both the atmosphere and the scrubbers, a great deal of our attention was focused on the low pH catalyzed reaction. We also considered the high pH uncatalyzed SO_2 oxidation for which very few reliable data have been obtained in the past. Better understanding of the characterisitcs and mechanism of both the uncatalyzed and catalyzed oxidation of SO_2 in aqueous solution should lead to improved efforts of controlling the effects of this reaction. This work is the initial part of an overall study of SO_2 oxidation kinetics in all pH ranges.

II. PREVIOUS KINETIC WORK ON LIQUID-PHASE OXIDATION OF SULFUR DIOXIDE

Although many authors do not specifically mention the pH at which their experiments were done, the kinetic work on SO_2 oxidation can clearly be divided into two groups: the low pH oxidation (pH<5) and the high pH oxidation (pH>7). A lot of kinetic experiments have been performed at low pH with the purpose of extrapolating the results to the atmospheric oxidation of SO_2 in cloud, fog and rain droplets. Most of the work at high pH (sulfite oxidation) has been done to facilitate measurements of interfacial areas in gas-liquid contactors. If the kinetics of a reaction is known, interfacial areas can be calculated from the theory of gas absorption accompanied by a chemical reaction. Sulfite oxidation kinetics is also used for evaluating the performance of aerobic fermentors.

Low pH Oxidation

Uncatalyzed SO_2 oxidation at low pH has received little attention since it occurs at very slow rates. Hoather and Goodeve[22] found that, with SO_2 present initially at 0.01 N, the time required for the reaction to go halfway to completion at 40°C was of the order of ten days. However, low pH oxidation of SO_2 can be very effectively catalyzed by metal salts, and the influence of a large number of catalysts has been studied extensively. There are two common methods for obtaining kinetic data for the catalyzed SO_2 oxidation at low pH: kinetic studies in bulk solution and absorption studies, either in water droplets containing catalyst or in packed columns.

Hoather and Goodeve[22] used a dilatometric technique to follow the bulk phase oxidation of sulfur dioxide at 35°C, with manganous sulfate as the catalyst. SO_2 concentration was in the range 0.0005 - 0.005 M, while oxygen concentration was of the order of 10^{-4} M. Catalyst concentration varied from 3×10^{-6} M (0.5 p.p.m. by weight) to 8×10^{-5} M (12 p.p.m.). They found that the reaction was zero order in both SO_2 and oxygen until concentrations of either dropped below about 1.25×10^{-5} M. The rate was proportional to the 1.7 power of the catalyst. Addition of sulfuric acid reduced the rate of reaction although it remained zero order. For unexplained reasons, the acid formed by the reaction did not slow the reaction and cause its graph to curve away from zero order line. By making several runs at 30°C, an activation energy of 27,300 calories was determined.

Bassett and Parker[5] bubbled a mixture of SO_2 and O_2 through solutions of various salts for several hours at 25°C. SO_2 reached high concentrations in solution, while the catalyst concentration in various runs ranged from 10^{-3} M upward. Results are difficult to interpret because there is no basis for deciding whether the reaction rate was limited by the resistance to mass transfer. Manganese salts were the most potent catalysts, being many times more effective than cobalt and nickel salts. Sulfates of these metals were quite a bit more efficient than chlorides. Ferric and cupric salts were also active as catalysts. $MgSO_4$, $ZnSO_4$, NH_4Cl and NaCl were ineffective. Hydrochloric acid reduced the rate only slightly for concentrations up to 0.1 M, but it retarded the reaction remarkably at higher concentrations. This reduction in rate is attributed to decreased oxygen solubility at large ionic strength.

Johnstone and Coughanowr[24] studied the kinetics of the liquid-phase oxidation by mixing solutions of SO_2 with solutions of oxygen containing $MnSO_4$ and quenching the reaction after fixed intervals of time by pipetting samples into standard iodine to determine the amount of SO_2 remaining. Initial SO_2 concentration was around 0.002 M, while oxygen concentration varied slightly around 0.0005 M. Catalyst was present at 4-14 p.p.m. Temperature was 25°C. The rate of reaction always remained constant until the oxygen content was essentially depleted. The apparent zero-order reaction constant was found. When sulfuric acid was not present in the solution initially, the rate constant was proportional to the square of $MnSO_4$ concentration. When sulfuric acid was added to the catalyst solution before mixing, the initial rate decreased as the acid concentration increased. The initial apparent zero-order reaction rate constants were found for several concentrations of externally added acid at a $MnSO_4$ concentration of 12.5 p.p.m. As in the case of Hoather and Goodeve[22], the sulfuric acid formed by SO_2 oxidation itself did not appear to slow the reaction down. Iron sulfate was found to be several orders of magnitude less effective than $MnSO_4$, while $NiSO_4$ at 1000 p.p.m. did not show any catalytic action.

Junge and Ryan[28] bubbled dilute mixtures of SO_2 (5-200 p.p.m. by volume) in air through different 1 p.p.m. catalyst solutions to investigate the formation of sulfate. Their results showed that oxidation did not take place significantly without a catalyst; there was also no noticeable increase in the reaction rate with MaCl present. Of the salts examined $McCl_2$ was the most effective catalyst, followed by $CuCl_2$, $FeCl_2$ and $CoCl_2$. The authors found that formation of sulfate is highly dependent on the pH of the solution in the pH range 1-5. As the pH decreases by the formation of sulfuric acid from SO_2 oxidation, the production of sulfuric acid slows down and finally stops. A decrease in pH by addition of hydrochloric or citric acid causes similar effects—lower final concentrations of sulfuric acid are produced. Junge and Ryan concluded that the major factor which restricts sulfate formation is the hydrogen ion concentration.

Johnstone and Moll[25] used fog chambers to study the production of H_2SO_4 when high humidity SO_2 fogs were exposed to nuclei of oxidation catalysts. The effect of manganese and iron salts was investigated. Manganese was found to be the better catalyst. Sodium chloride did not catalyze the reaction at all.

Pritchett[40] mixed a solution of dissolved oxygen with a solution of sulfur dioxide containing manganese sulfate catalyst in a continous flow reactor. The completion of reaction was measured by the rise in temperature using a thermistor detector. SO_2 concentration varied from 0.01 to 0.15 M, oxygen from 10^{-3} to 10^{-4} M, while $MnSO_4$ concentration was unusally high — 0.01 to 0.25 M. Oxidation of SO_2 occurred at an unusual accelerating rate. This was attributed to the formation of a catalytic complex by an autocatalytic reaction. Oxidation proceeded at a rate proportional to the concentration of the active catalyst and the square root of the oxygen concentration. This behavior, not observed by anyone else was probably due to extremely high catalyst concentrations. Sulfuric acid did not have any significant effect on the rate of the reaction, even when it was added at a concentration which was 15 times greater than that which would be produced by the reaction itself.

Conghanowr and Krause[10] examined the rate of oxidation of sulfur dioxide in a solution of manganous sulfate over a broad range of catalyst concentration. Initial sulfur dioxide concentration was around 0.002 M, while the oxygen concentration in solution varied from 0.3 to 0.7 x 10^{-3} M. Up to 15 p.p.m. catalyst concentration a batch method was used; from 100 to 10,000 p.p.m. a flow method was applied. The reaction was zero order with respect to both sulfur dioxide and oxygen at all concentrations of $MnSO_4$ used. The concentration of manganous sulfate had a large effect on the rate of reaction; from 0 to 100 p.p.m., the reaction rate constant, k_o, is proportional to the square of the catalyst concentration, but above 100 p.p.m., k_o increases less rapidly up to about 500 p.p.m., after which it increases very slowly with catalyst concentration. The reaction was easily inhibited by very small amounts of contaminant.

Matteson, Stober and Luther[32] studied the kinetics of the oxidation of SO_2 in aqueous aerosols of $MnSO_4$. They observed that the rate of reaction decreased with increasing amounts of sulfuric acid formed. A decrease in pH slowed and eventually halted the reaction. A four-step mechanism, involving intermediate complexes with the catalyst, was proposed.

Commenting on iron and manganese catalyzed reactions, Foster[14] concludes that it is the pH conditions existing at the beginning of the experiment which determine the subsequent rate of oxidation. Discussing the retarding effect of H_2SO_4 on the rate of reaction catalyzed by manganese, he mentions the work of Grozdovskii[19] and Kashtanov and Ruizthov[29], which indicated that the reaction rate is reduced with time as a result of part of the manganese forming a stable complex with the sulfuric acid. Foster suggests that at the low concentrations of $MnSO_4$ and H_2SO_4 used by Hoather &

Goodeve[22] and Johnstone & Coughanowr[24], this complexing reaction takes places so slowly that very little complexing occurs in the time of the experiment.

Gunn and Saleem[20] studied the kinetics of the absorption of sulfur dioxide and oxygen and the catalyzed liquid phase oxidation of SO_2 in a co-current gas-liquid contactor packed with glass fibers. Using the steady-state theory of absorption accompanied by a chemical reaction, the reaction kinetics are deduced from SO_2 absorption rates. Partial pressures of SO_2 and O_2 in the gas varied from 0.003 - 0.02 atm and 0.09 - 1 atm respectively. The concentration of manganous sulfate catalyst in the liquid phase was maintained at 0.01 M (around 1500 p.p.m.). Order of reaction with respect to oxygen was found to be zero, while the order in SO_2 was zero if P_{SO_2} is high enough (if not, there is a small positive dependence on SO_2 concentration). An increase in sulfuric acid concentration, obtained by recirculating the liquid in the contactor and building up H_2SO_4, decreased the reaction rate. The authors presented a graph showing the zero order reaction rate constant as a function of acid concentration.

Cheng, Corn and Frohliger[8] studied the reaction kinetics of water soluble aerosols and SO_2 in air at p.p.m. concentrations. A steady-state in the aerosol droplet absorption and oxidation of SO_2 was attained in which, according to the authors, $SO_2 \cdot H_2O$ (unionized form) combines with metal ions to form an intermediate complex. $MnSO_4$ was about four times more effective in catalyzing the reaction than $MnCl_2$ or $CuSO_4$.

Walter[52] was the only one who studied catalyzed SO_2 oxidation kinetics in bulk solutions by employing a continous supply of oxygen. However, for a very effective catalyst like $MnSO_4$, he could not get oxygen into the solution fast enough, so that his reactions were limited to the oxygen initially present in to SO_2 solution. The catalysts used were $MnSO_4$ (1.6 - 6 p.p.m.), $MgSO_4$ (1000 - 18,000 p.p.m.), $ZnSO_4$ (4000 - 20,000 p.p.m.), $CaSO_4$ (20 - 120 p.p.m.). In all runs the initial SO_2 concentration was around 0.002 M (pH$\sim$2.7) and the oxygen about 0.006 M. Temperature was kept constant at 25°C. A zero order reaction was obtained in all cases. Relatively good agreement with the results of Johnstone and Coughanowr[24] for $MnSO_4$ catalyst was obtained. The reaction rate constant depended on the 1.9 power of $MnSO_4$ concentration. For $MgSO_4$, $ZnSO_4$ and $CaSO_4$, the power dependence of k_o on the catalyst concentration was 0.71, 0.73 and 0.39 respectively, but not enough points were obtained to confirm these values more definitely. $MnSO_4$ appeared to be at least three orders of magnitude more effective than the other catalysts.

In recent work, Powell[39] and Ness[35] focused their attention on the uncatalyzed oxidation of aqueous solutions of bisulfite, with the hope that the information obtained by their approach would yield a firmer basis for understanding the chemistry, kinetics and mechanism of more complicated SO_2 systems. The reaction was studied in the pH range 1.2 - 1.7. The rate of oxidation was found to be first order in bisulfite ion concentration. Powell's first order reaction rate constant was 0.061 hr^{-1}, while Ness, using more realistic

expressions for the activity coefficients of the sulfur dioxide-bisulfite equilibria, obtained a value of 0.0065 hr^{-1}.

In most of the work presented, the pH values of the solution in the course of experiments were not given, but since in most cases the initial concentration of sulfurous acid was of the order of 10^{-2} - 10^{-3} M, we can assume that the pH was below 4. It is obvious that manganese salts are by far the best catalysts for SO_2 oxidation at these low pH values. The reaction appears to be zero order with respect to SO_2 concentration, no matter what catalyst is used. The zero order dependence in oxygen, observed by many authors, might me questionable because in most experiments the initial oxygen concentration did not vary much, and in all cases oxygen was present in very small amounts and was the limiting reactant.

High pH Oxidation

High pH SO_2 oxidation occurs at higher rates than low pH oxidation due to the presence of sulfite which reacts very rapidly with oxygen, especially in the presence of catalysts. Methods employed in studying this process include bulk kinetic experiments, usually rapid-mixing techniques in flow reactors, and absorption studies, either in wetted-wall columns or in mechanically agitated sulfite solutions.

The experimental work on the uncatalyzed sulfite oxidation and the numerous problems that various workers had with it be will be described in Section IV.

The only two catalysts for which high pH kinetic data are available are cobaltous (CO^{++}) and cupric (Cu^{++}) ions. Absorption of oxygen in Na_2SO_3 solutions in the presence of $CoSO_4$ as catalyst is particularly useful in evaluating interfacial areas of gas-liquid contactors. The reaction kinetics have to be well known in order that the theory of absorption with chemical reaction could be used for this purpose. Interfacial areas have to be measured at high chemical enhancement factors of the absorption process in order to eliminate the influence of hydrodynamic conditions at the gas-liquid interface on the absorption rate. Cobalt-catalyzed sulfite oxidation proceeds at extremely fast rates, satisfied the above requirements, and has therefore been the subject of a great deal of research. Cobalt is a more powerful catalyst than copper (at least two times according to Westerterp et al.[54]) and data for cobalt are more reproducible than those for copper.

The reaction has very complex kinetics; for instance, according to Astarita et al.[2], it is zero order in O_2 when the sulfite concentration is 0.06 M; first-order when it is 0.25 M and second-order when it is 0.25 - 1 M. Reith and Beek[43] reviewed most of the data on cobalt catalysis obtained by absorbing oxygen in Na_2SO_3 solutions. For $0.21 < P_{O_2} < 1$ atm, $15^{o}C < T < 60^{o}C$, 3×10^{-6} M $< (Co^{++}) < 3 \times 10^{-3}$ M, $7.5 < pH < 8.5$ and 0.4 M $< (SO_3^{=}) < 0.8$ M, most investigators agree that the reaction is second order in oxygen, first order in cobalt and zero order in sulfite. Using the absorption method at low Na_2SO_3 concentrations

(0.002 - 0.07 M), Yagi and Inoue[56] found the reaction to be first order in oxygen, first order in sulfite and first order in cobalt (at cobalt concentrations of 5×10^{-8} - 6×10^{-7} M).

Fuller and Crist[16] found that copper catalyst greatly affects the sulfite oxidation rate even at concentrations as low as 10^{-8} M. This reaction, as well as the cobalt-catalyzed one, has been studied by several researchers who used the rapid-mixing flow method of Hartridge and Roughton[21]. Aqueous solutions of oxygen and sodium sulfite were passed through a rapid mixer, and the extent of reaction was followed by the temperature rise of the reacting stream in an observation tube following the mixer. Barron and O'Hern[4] used sulfite concentrations of 0.05 - 0.5 M and cupric ion concentration of 10^{-9} - 10^{-4} M. The reaction order was zero in oxygen, 3/2 in sulfite and 1/2 in catalyst. Chen and Barron[7], working at a pH of 9, obtained the same orders when cobaltous ion was used at concentrations of 10^{-7} - 10^{-6} M. Srivastava, McMillan and Harris[47] worked with cobaltous ion at 10^{-5} - 10^{-4} M, the pH of the solution being 8.3. They obtained an oxygen order of one, cobalt order of one, and sulfite order of zero for $(SO_3^=) > 0.04$ M. For $(SO_3^=) < 0.02$ M, there was a marked deviation from zero order. A couple of mechanisms were proposed by all these researchers, one involving a free-radical chain and one involving the formation of a cobalt complex with sulfite.

It is obvious from the above review that the order of reaction with respect to both oxygen and sulfite changes with sulfite concentrations. It has been established that cobalt is a more potent catalyst than copper, but nothing is known about other metal catalysts. Considering the results of low pH catalyzed oxidation of SO_2, experiments with manganese catalyst at high pH should be very valuable.

III. LOW pH CATALYZED OXIDATION OF SULFUR DIOXIDE

In this part of our work, we focused our attention on two catalysts: magnesium and manganese. Magnesium is present in large quantities in many SO_2 scrubbing systems, but any conclusions regarding its catalytic action have yet to be made. Of all the catalysts studied, manganese has been shown to be the most effective one by far, and is therefore very suitable for studies of the influence of various factors on the catalyzed SO_2 oxidation rate.

All of our experiments were conducted in the pH range 1 - 4, where bisulfite is the predominant SO_2 species in solution. Therefore, we actually studied the catalyzed oxidation of bisulfite. Of the factors which could influence the rate of oxidation, we examined the effects of varying the pH, increasing the sulfate concentration, and slightly altering the ionic strength. From these effects and the observed order of reaction, certain conclusions could be made about the manganese-catalyzed oxidation of SO_2.

Experimental Apparatus

The experimental apparatus consisted of a reaction flask and associated connections, oxygen supply, thermostat (see Fig. 2) and titrametic analysis equipment.

The reaction flask was a three-neck, 1-liter Pyrex flask, modified by four indentation baffles and a flattened bottom to accommodate a 5-cm. teflon-coated magnetic stirring bar. The same flask was utilized for all experiments dealing with catalyzed liquid-phase oxidation of SO_2.

One fitting was a teflon-stoppered 25-ml. burette for the addition of catalyst solution, with the tip sealed in a 24/40, tapered, ground-glass joint. A pressure equalizing side-arm was attached to the burette for operating at a slight gauge pressure, which served to increase the available oxygen for the reaction, to eliminate the possibility of any leaks into the flask, and to facilitate sample-taking. A three-way teflon stopcock was located between the side-arm and the burette.

The second fitting was a capillary glass tubing through which samples of solution from the flask were taken. It was sealed in a 24/40, tapered, ground-glass joint such that the bottom of the tubing cleared the top of the magnetic stirring bar by approximately one centimeter. A male glass

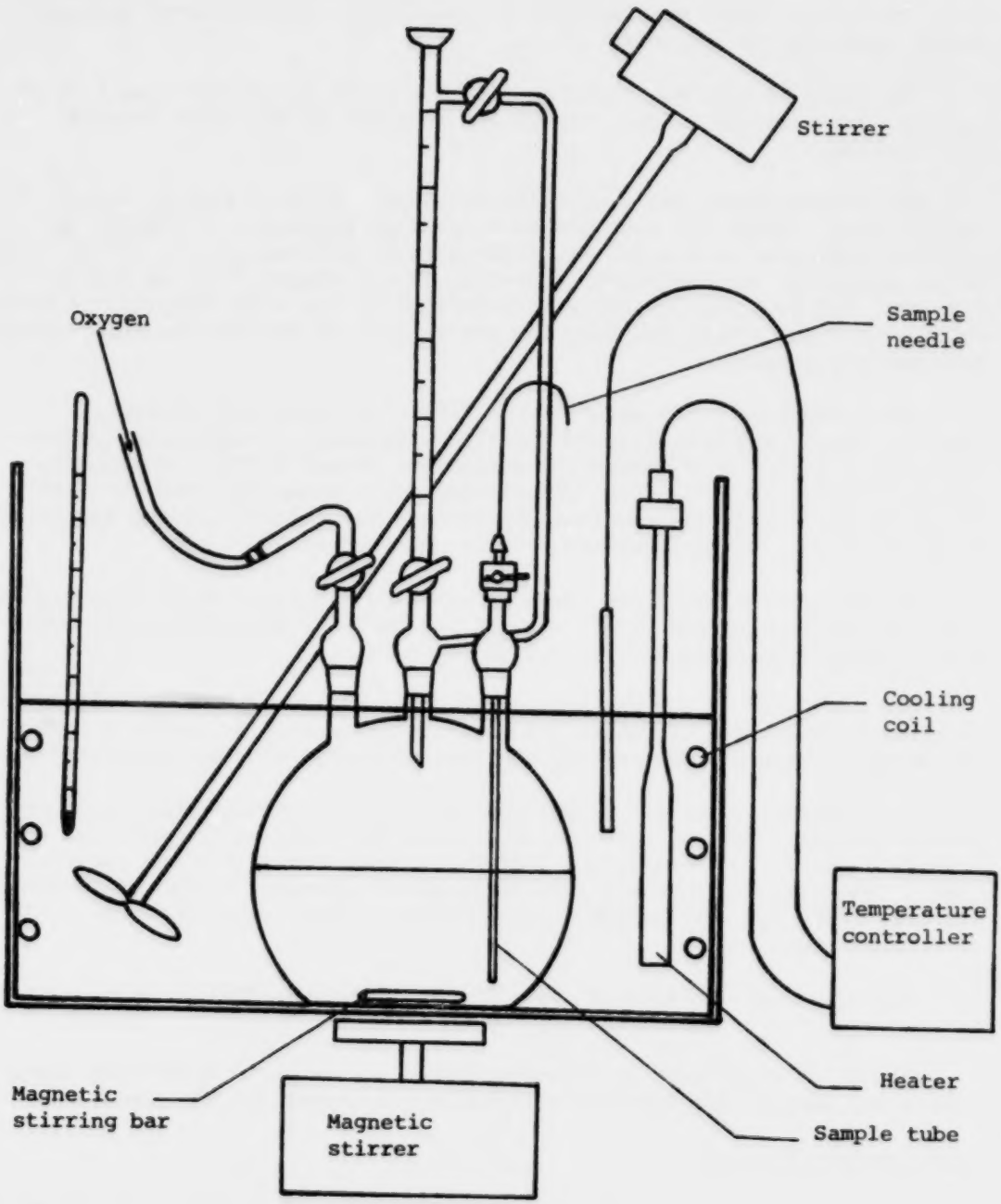


Fig. 2. Experimental apparatus.

Luer joint was connected to the top of the caplillary tubing. A stainless steel valve (B-D MSO1) was fastened to this joint, with a curved syringe needle connected to the valve.

The third fitting was a teflon stopcock which was sealed into a 24/40, tapered, ground-glass joint. Oxygen was supplied to the flask through this fitting.

The oxygen supply was a cylinder of oxygen, Linde Division, Union Carbide Corp. After the high pressure cylinder regulator, a Foxboro low pressure regulator (1.7×10^6 Pa. maximum inlet pressure, 4.1×10^5 Pa. maximum outlet pressure) was connected in series. Tygon tubing, 0.64 cm inside diameter, led from the low pressure regulator to the third fitting. A second section of Tygon tubing led from the outlet side of the low pressure regulator to a mercury manometer.

The thermostat was a water-filled Plexiglas tank with stirrer, heating element and auxiliary coil for cooling-water. Temperature was controlled to within $\pm$ 0.01°C by a Thermotrol controller (model 1053A). A magnetic stirrer capable of 1850 r.p.m. was mounted close under the tank in order to continuously stir the reactants by turning the teflon stirring bar in the reaction flask. The stirrer was usually operated at 900 r.p.m.

To measure the pH of the reacting solution a Corning Model 10 expanding-scale pH meter, equipped with a combination AgCl-KCl electrode, was used. The accuracy is estimated to be $\pm$ 0.02 pH units.

The main part of the titrametric analysis equipment was a special 5-ml burette, on which the titration end-point could be read to within 0.002 ml. The analysis used for determining SO_2 concentrations will be described later.

The chemicals used for titrations, the catalyst salts ($MgSO_4$ and $MnSO_4$), sodium hydroxide and hydrochloric acid (used for changing the pH), and sodium sulfate (used for increasing the sulfate concentration) were all reagent grade. Magnesium sulfate was from Mallinchrodt Chemical Works, while manganese sulfate, $MnSO_4 \cdot H_2O$, and sodium sulfate, $Na_2SO_4 \cdot 10H_2$), were from the J. T. Baker Chemical Co.

All necessary weighing of chemicals was done on a Mettler or an Ainsowrth balance of $\pm$ 0.0001 gm sensitivity.

Deionized water used in the experiments was obtained from Roger Adams Laboratory supply; its specific resistance was around 400,000 ohm-cm.

Experimental Procedure

Prior to each experiment, the reaction flask and associated fittings were cleaned with a concentrated potassium dichromate cleaning solution ($H_2SO_4 + K_2Mn_2O_7$)

and rinsed many times with deionized water.

Before the start of a run 375 ml. of sulfur dioxide solution and the stirring bar were placed in the flask. The SO_2 solution of desired concentration was obtained by diluting a 1 M SO_2 solution with deionized water. The 1 M solution was prepared by bubbling sulfur dioxide gas in deionized water. SO_2 gas was standard grade supplied from cylinders obtained from the Linde Division of Union Carbide Corp.

The fittings were attached to the flask necks, the joints being sealed with teflon sleeves to insure purity, and the Tygon tube leading from the oxygen supply was connected to the oxygen inlet. The flask was then placed in the constant temperature bath.

The temperature of the water bath was adjusted to 25.00°C and was measured to $\pm$ 0.01°C accuracy by a thermometer calibrated by the National Bureau of Standards

Oxygen was blown through the reaction flask for several minutes to purge the air. The pressure was then set a 800 mm Hg, the magnetic stirrer was turned on, and a couple of hours were allowed for oxygen absorption.

To actually start a run, the catalyst solution was placed in the burette, the oxygen inlet stopcock was closed, while the stopcock on the pressure equalizing arm of the burette was opened. Then the burette stopcock was opened to let 25 ml. of catalyst solution into the flask (the concentration of the catalyst solution was so adjusted that additional of 25 ml. to the 375 ml. of SO_2 solution in the flask resulted in the desired p.p.m. of catalyst). Both stopcocks on the burette were then shut and the oxygen pressure again adjusted to 800 mm Hg by opening the oxygen inlet stopcock. Stirrer speed was set at 900 r.p.m.

The first sample was taken a few minutes after the catalyst was added, while other samples (usually 10 - 15 ml.) followed after desired time intervals. The change in SO_2 concentration in the flask was thus followed as a function of time. Prior to each sample-taking, the sampling lines were purged by letting several milliliters of SO_2 solution out. The solution flowed through the lines readily when the valve was opened since the system in the flask was under slight gauge pressure. pH measurements were made several times in the course of the reaction by drawing a number of 5-ml. samples and measuring acidity with a pH meter which was previously calibrated against a known standard. These samples were used only for pH measurements and were not titrated.

SO_2 concentration of a sample (or more precisely, the total sulfur concentration in the +4 oxidation state) was measured by quenching a known volume of reactant solution in an iodine solution of known volume and concentration. The iodine reacts with the various SO_2 species in solution to form sulfate ions according to the following reactions:

$$SO_2 \cdot H_2O + I_2 + H_2O \rightleftharpoons SO_4^{=} + 2I^- + 4H^+ \quad (3)$$

$$HSO_3^- + I_2 + H_2O \rightleftharpoons SO_4^{=} + 2I^- + 3H^+ \quad (4)$$

$$SO_3^{=} + I_2 + H_2O \rightleftharpoons SO_4^{=} + 2I^- + 2H^+ \quad (5)$$

The excess iodine was then determined by titration with arsenious acid.

$$H_3AsO_3 + I_2 + H_2O \longrightarrow H_3AsO_4 + 2I^- + 2H^+ \quad (6)$$

Since reactions (3), (4) and (5) are pH-dependent, sodium bicarbonate was used as a buffer to increase the pH and force the reactions to completion. All reagent solutions were approximately 0.1 N (or diluted further) and were prepared and standardized by standard methods[46].

A sample calculation of the total SO_2 concentration in the flask at a particular time is shown in Appendix A. The time necessary to take a sample and quench it was less than one minute.

A special advantage of our experimental method is the continuous oxygen supply during the course of the reaction. All other investigators either worked with only the oxygen that was initially dissolved in the SO_2 solution (0.0012 M at 25°C and 1 atm. oxygen pressure)[37] or could not get oxygen into the solution fast enough (i.e., the process was mass-transfer controlled). Due to good stirring, the process in our system was not mass-transfer controlled, which was shown by calculating the activation energy from runs at 25 and 38°C. This fact enabled us to feed the oxygen to the solution and sustain the reaction for several hours, sometimes even days. The time scale in most of the previous experimental works on catalyzed oxidation of SO_2 at low pH values was of the order of second or minutes, depending on the catalyst concentration.

In most of our experimental runs, the total SO_2 (or the total sulfur concentration in the +4 state) was between 0.01 and 0.02 M, giving an initial pH of the solution of about 2.2 - 2.3. For runs at higher pH, we added drops of 1 N NaOH to the solution prior to the start of the reaction. The pH was raised to around 4 with 2.7 ml. of 1 N NaOH added to 375 ml. of SO_2 solution. To obtain pH values below 2.2, we added certain amounts of 1 N HCl. Twenty-five ml. of 1 N HCl, added to 375 ml. of reactant solution, have a pH of approximately 1. In experiments in which the initial sulfate concentration in the reacting solution was increased, sodium sulfate was added to the initial 375-ml. volume in desired amounts, and ample time was allowed for it to dissolve completely. NaOH and Na_2SO_3 were used in the experiments since sodium was shown to have no catalytic effect on SO_2 oxidation.

Results and Discussion

We first studied the catalytic action of magnesium sulfate. In several SO_2 scrubbing processes magnesium ion is present in large quantities in the scrubbing solution; therefore, we worked with a very high $MgSO_4$ concentration — 20,000 p.p.m. (0.17 M). We observed a zero-order reaction with respect to SO_2 concentration, with the reaction rate constant, k_o, having a value of 1.11×10^{-4} moles/lit. hr. (see Fig. 3).

We also made a run for the uncatalyzed reaction at the same initial SO_2 concentration. This run showed that 0.001 moles/lit. of SO_2 reacted in 15 hours. Comparing these numbers with the reaction shown in Fig. 3, we can see that 20,000 p.p.m. $MgSO_4$ in solution speeds up the reaction only about 60% over the uncatalyzed case. Since this is a rather small enhancement of the reaction rate at a very high catalyst concentration, we conclude that $MgSO_4$ is a poor catalyst for the bisulfite oxidation.

Bassett and Parker[5], using solutions saturated in sulfur dioxide, found that magnesium retarded the reaction at high concentration (above 0.05 M). Our result does not agree with their findings. However, in the $MgSO_4$ that we used, there was 0.001% manganese which could account for part of the catalytic action since Mn is a very good catalyst.

Walter[52] found that the catalytic action of calcium sulfate is roughly the same as that of $MgSO_4$, while zinc sulfate was only 50% as effective. In light of our result, we can state that Ca, Mg and Zn, all of which can be present in scrubbing solutions in large quantities, are not very effective from the standpoint of catlyzing the undesirable SO_2 oxidation to sulfate.

As already noted, many investigators found manganese sulfate to be a very effective catalyst for bisulfite oxidation. Having this in mind, in our studies of the manganese-catalyzed reaction, we used low catalyst concentrations — 1 and 3 p.p.m. $MnSO_4$ (6.62×10^{-6} M and 1.99×10^{-5} M respectively). The reaction was found to be zero order with respect to the SO_2 concentration (i.e., total sulfur concentration in the +4 state). The reaction rate constants were 2.5×10^{-4} moles/lit. hr. for 1 p.p.m. catalyst (Fig. 4), and 10.6×10^{-4} moles/lit. hr. for 3 p.p.m. catalyst (Fig. 5). Initial SO_2 concentrations in both of these cases were around 0.012 M. However, the same reaction rate constants were obtained when the initial SO_2 concentration was almost an order of magnitude smaller around 0.002 M (Fig. 6 shows the case for 1 p.p.m. $MnSO_4$). We could not find a value for k_o at 1 or 3 p.p.m. $MnSO_4$ in any of the articles described in Section II because none of the authors used such low manganese concentrations. However, if Johnstone & Coughanowr's[24] or Coughanowr & Krause's[10] results, obtained for $MnSO_4$ concentrations above 4 p.p.m., were extrapolated to 3 p.p.m. by assuming a second order dependence of k_o on the catalyst concentration, a value of 9.6×10^{-4} moles/lit. hr. would be obtained. Our k_o of 10.6×10^{-4} moles/lit. hr. for 3 p.p.m. $MnSO_4$ is then in very good agreement with this value.

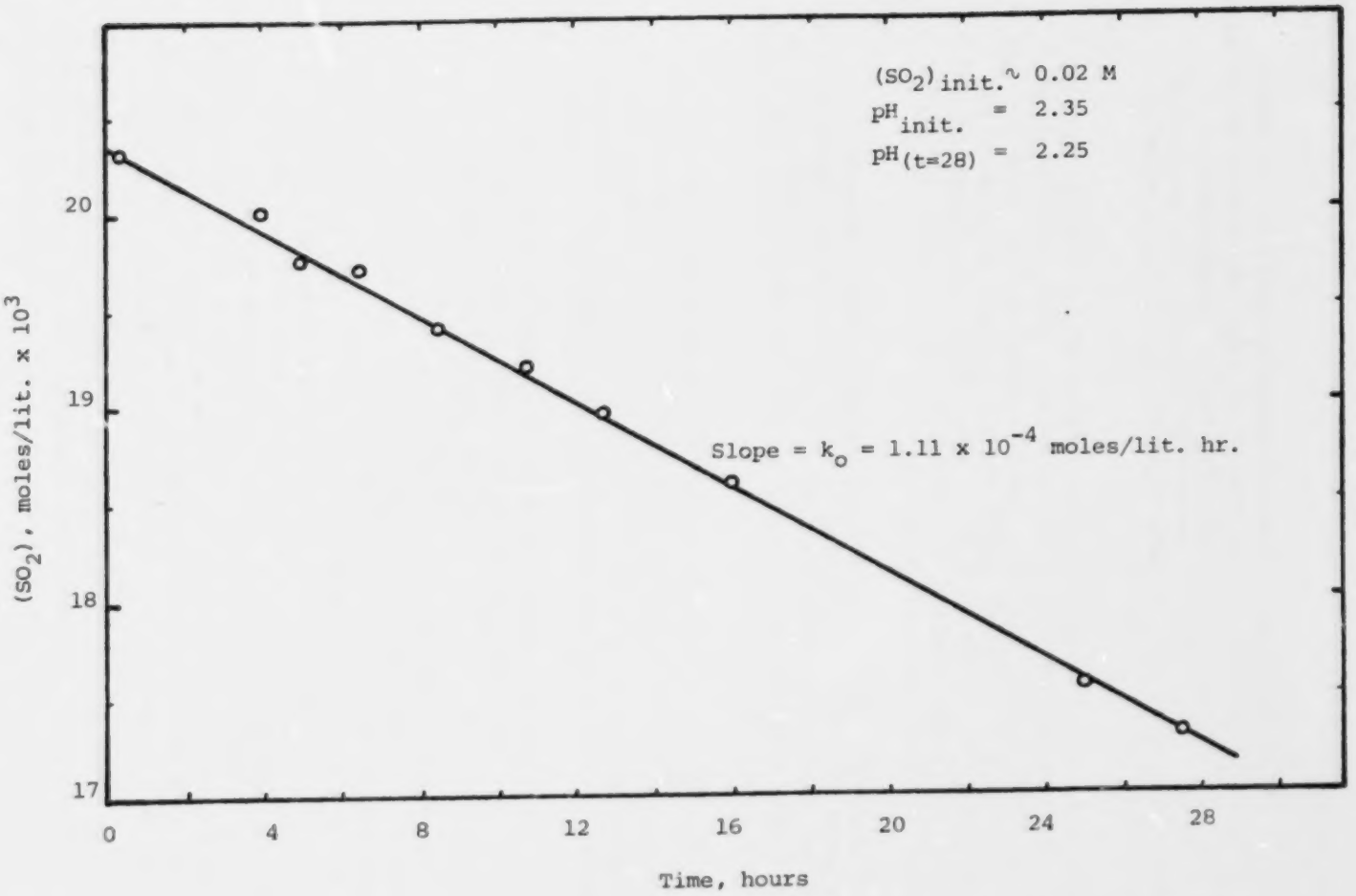


Fig. 3. SO_2 concentration as a function of time, with 20,000 p.p.m. $MgSO_4$ catalyst.

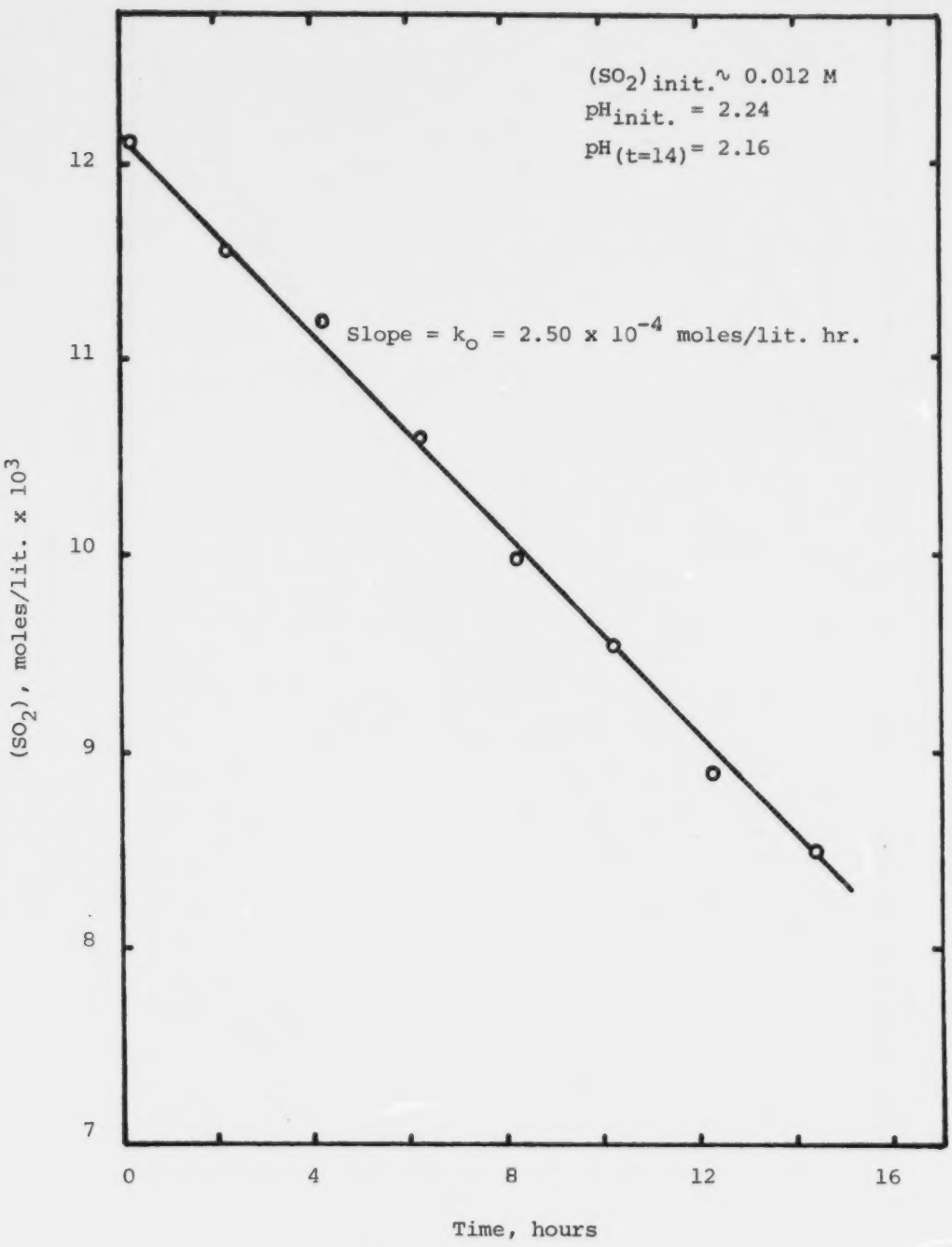


Fig. 4. SO_2 concentration as a function of time, with 1 p.p.m. $MnSO_4$ catalyst.

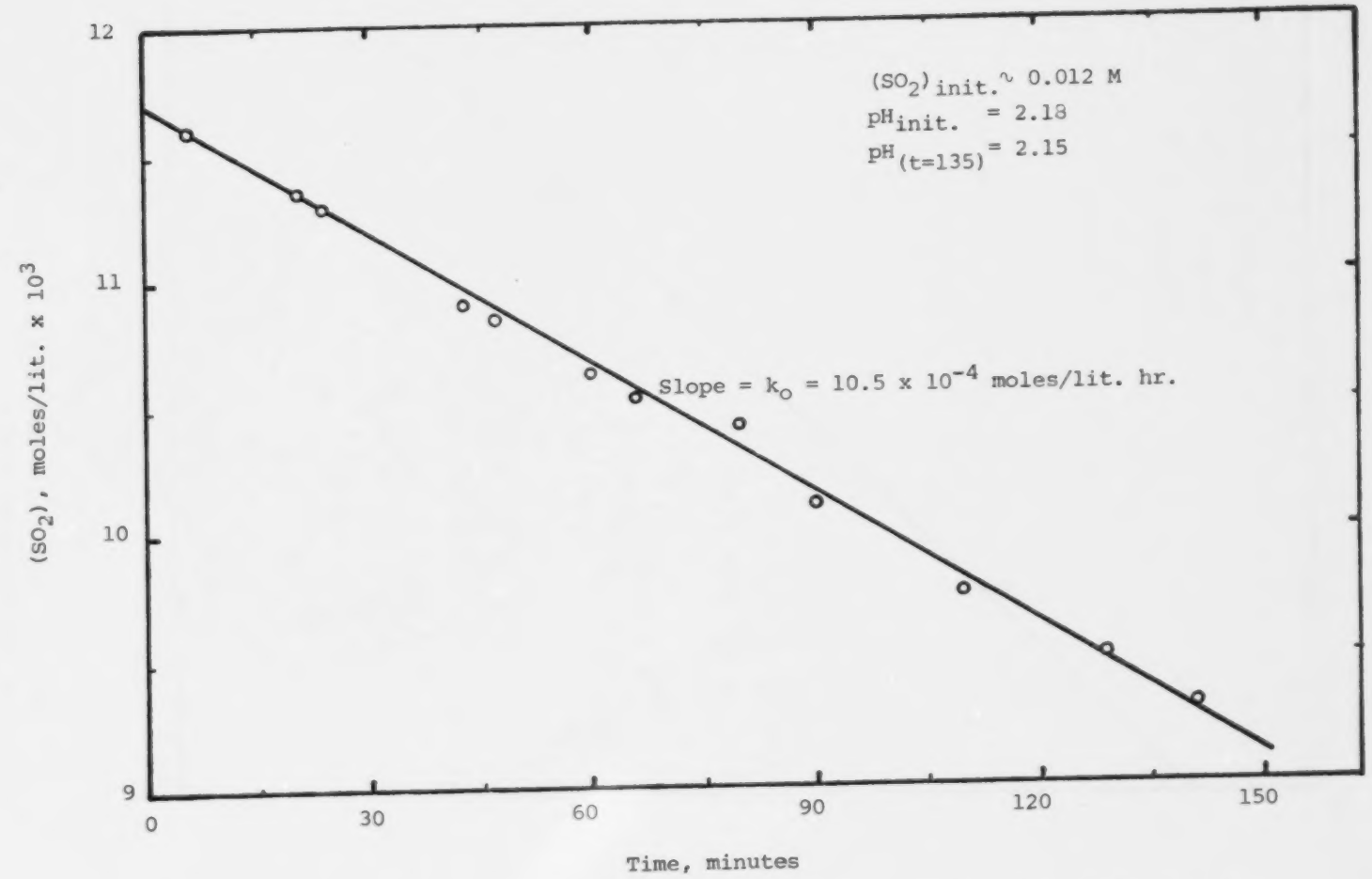


Fig. 5. SO_2 concentration as a function of time, with 3 p.p.m. $MnSO_4$ catalyst.

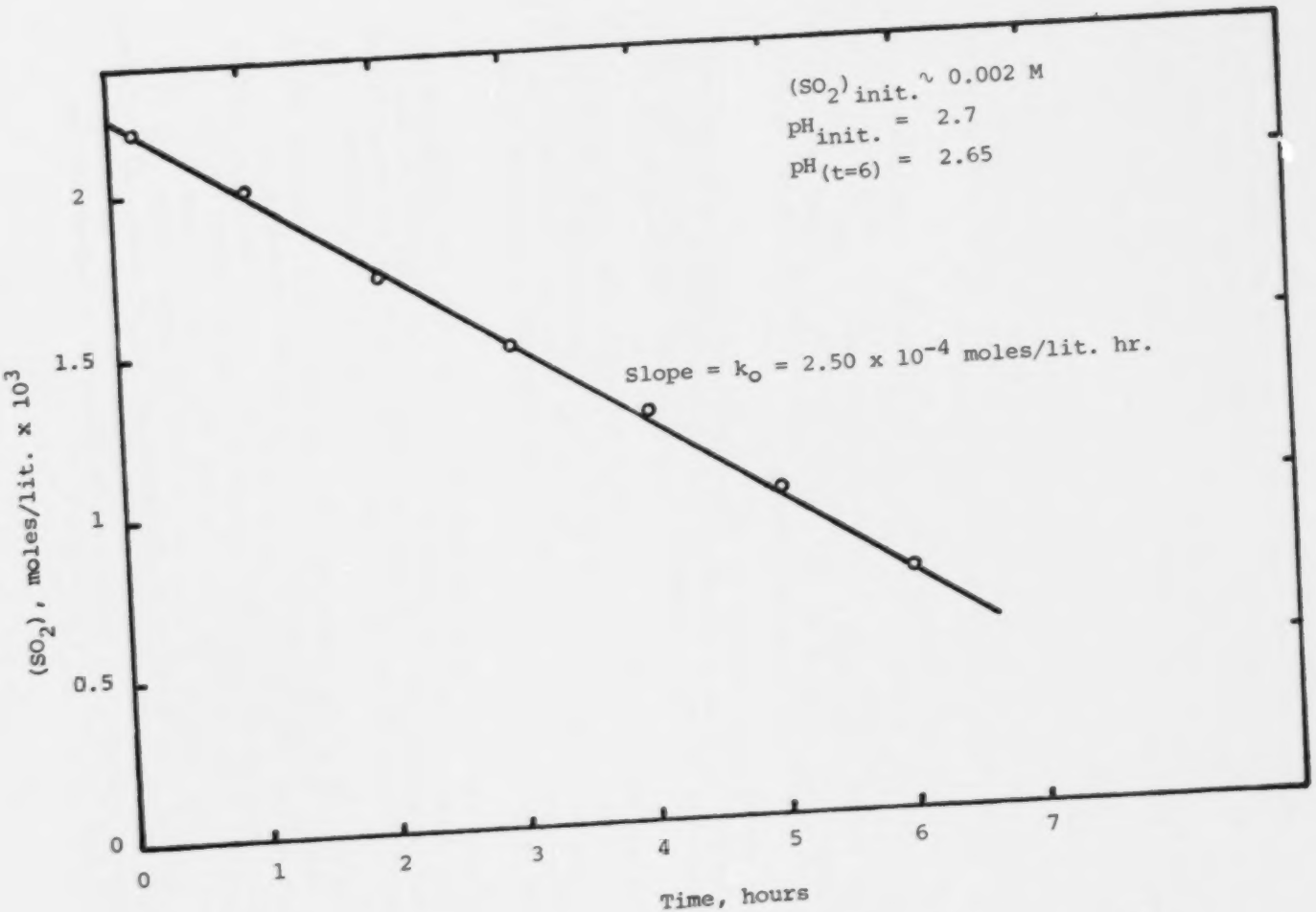


Fig. 6. SO_2 concentration as a function of time, with 1 p.p.m. $MnSO_4$ catalyst and lower $(SO_2)_{initial}$.

In order to make sure that we were obtaining purely kinetic results and that the reaction was not controlled by the rate of oxygen transfer to the solution, the activation energy for the $MnSO_4$-catalyzed reaction was calculated from the kinetic data at 25 and 38.2°C with 1 p.p.m. catalyst. The value for the activation energy obtained from $k_o = 2.5 \times 10^{-4}$ moles/lit. hr. at 25°C, and $k_o + 9.25 \times 10^{-4}$ moles/lit. hr. at 38.2°C, was 18.7 kcal/mole. This value is far too high for a mass-transfer limited process.

From our results it is clear that manganese is a very effective catalyst even when present at only several parts per million in solution. Three p.p.m. manganese sulfate in a scrubbing solution will cause 10 times higher SO_2 oxidation rate than 20,000 p.p.m. $MgSO_4$. It is very likely that manganese is present in the scrubbing liquid in p.p.m. concentrations.

We saw in Section II that several authors observed a zero order in oxygen for the catalyzed SO_2 oxidation at low pH values. In the same section (p. 8), we questioned the validity of such observations. In the case of our experimental results, the oxygen order cannot be determined since the oxygen concentration in solution was kept constant by the continuous supply of the gas and by efficient stirring of the reacting solution.

Neither manganese-catalyzed nor even magnesium-catalyzed SO_2 oxidation at high pH values could be followed in our experimental system since they were too rapid; all of SO_2 in solution reacted within several minutes.

In studying various factors which could influence the catalyzed SO_2 oxidation, we worked with $MnSO_4$ as catalyst since it is effective, and since even small changes in reaction rates can then be observed. The influence of pH was investigated first. As before, all experiments were done at 25°C and 800 mm Hg oxygen pressure.

As mentioned already, Junge and Ryan[28] observed that the production of sulfate by SO_2 oxidation was dependent on the pH of the solution in the range 1-5, and concluded that hydrogen ion concentration is the major factor which restricts sulfate formation. Foster[14] made similar conclusions.

We varied the pH of our reacting solutions from 1 to 4. Working with 1 and 3 p.p.m. $MnSO_4$, we found that the rate of bisulfite oxidation was independent of the pH. The results obtained from 1 p.p.m. manganese sulfate, with the initial SO_2 concentration of around 0.013 M, are shown in Fig. 7, while the reaction rate constants for 3 p.p.m. $MnSO_4$ and the same initital SO_2 concentration are plotted in Fig. 8. In both of these graphs, the pH values shown are the ones observed at the start of the reaction. All of these results, as well as those when the initial SO_2 concentration was almost in order of magnitude smaller, are summarized in Table 1. A representative run is shown in Fig. 9.

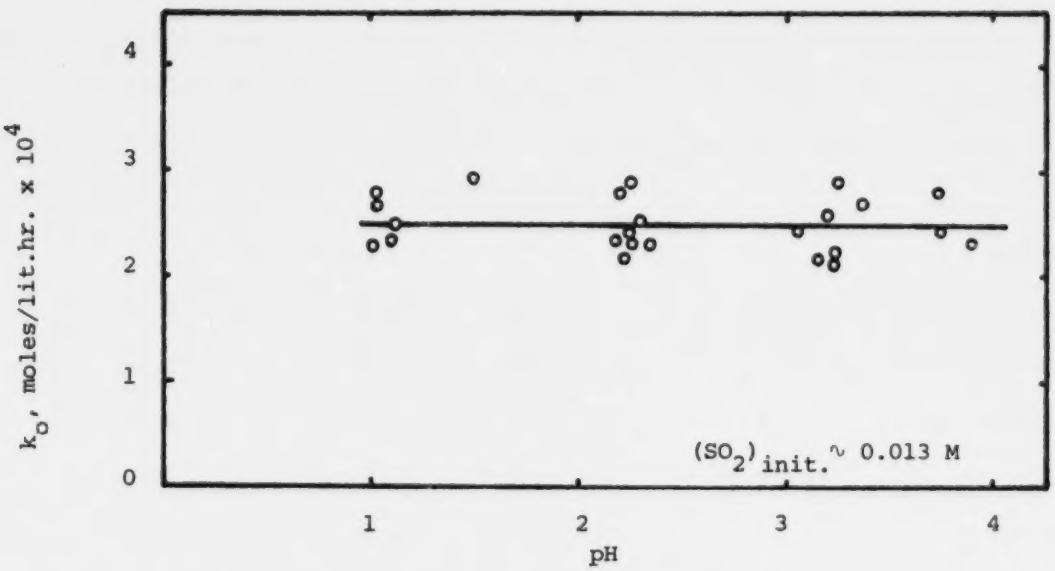


Fig. 7. Zero-order reaction rate constant, k_o, as a function of the initial pH, with 1 p.p.m. $MnSO_4$ catalyst.

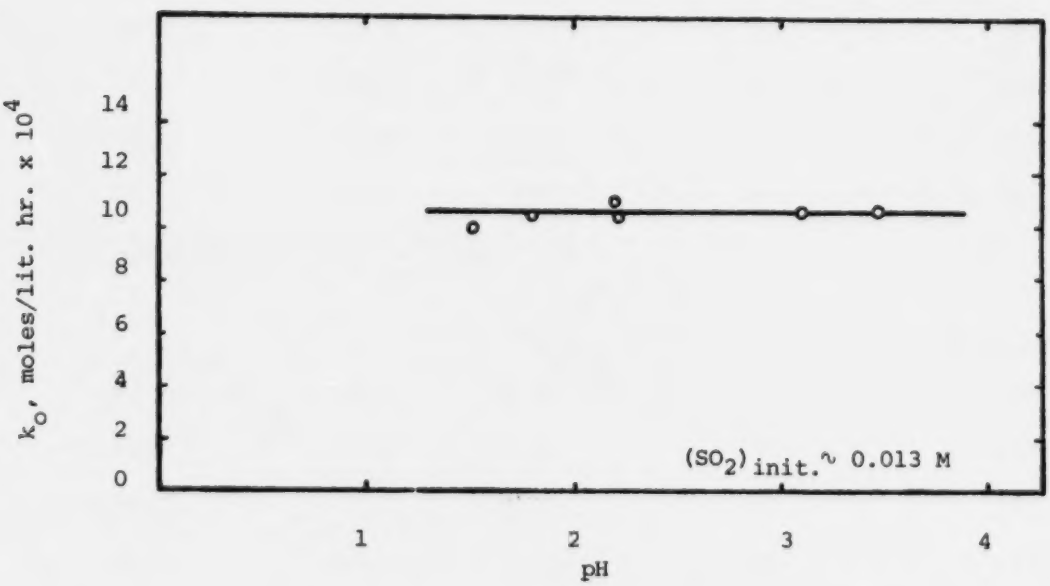


Fig. 8. Zero-order reaction rate constant k_o, as a function of the initial pH, with 3 p.p.m. $MnSO_4$ catalyst.

TABLE 1. Results of kinetic experiments at various pH values

$(SO_2)_{initial}$, M	Length of run (hr)	$pH_{initial}$	pH_{final}	k_o, moles/lit.hr. x 10^4
		1 p.p.m. $MnSO_4$		
pH ∿ 2				
0.013	15	2.19	2.12	2.84
0.010	14	2.30	2.15	2.55
0.010	14	2.26	2.13	2.90
0.011	12	2.18	2.13	2.36
0.009	14	2.24	2.16	2.50
0.012	11	2.22	2.15	2.20
0.011	11	2.27	2.20	2.40
0.008	7	2.33	2.26	2.32
0.002	4	2.7	2.65	2.60
0.002	4	2.7	2.65	2.20
0.002	6	2.7	2.65	2.50
0.002	6	2.7	2.65	2.60
			$k_{o(ave)}$ = 2.5 x 10^{-4} moles/lit.hr.	
pH ∿ 3-4				
0.012	20	3.15	2.70	2.20
0.011	20	3.22	2.77	2.25
0.011	15	3.09	2.70	2.45
0.010	12	3.22	2.82	2.90
0.009	12	3.75	2.98	2.45
0.009	11	3.37	2.90	2.70

(continued)

TABLE 1. (Continued)

$(SO_2)_{initial}$, M	Length of run (hr)	$pH_{initial}$	pH_{final}	k_o, moles/lit.hr. x 10^4
		1 p.p.m. $MnSO_4$ (Cont'd)		
pH ∿ 3-4 (Cont'd)				
0.010	20	3.20	2.83	2.20
0.011	12	3.74	3.00	2.83
0.011	12	3.21	2.90	2.60
0.013	15	3.90	3.05	2.35
0.002	6	3.65	3.35	2.45
			$k_{o(ave)}$ = 2.5 x 10^{-4} moles/lit.hr.	
pH ∿ 1				
0.013	7	1.03	1.00	2.80
0.013	7	1.03	1.01	2.30
0.011	12	1.49	1.40	2.95
0.012	15	1.08	1.03	2.35
0.013	14	1.01	0.99	2.70
0.012	14	1.10	1.04	2.50
0.002	7	1.75	1.73	2.60
			$k_{o(ave)}$ = 2.6 x 10^{-4} moles/lit.hr.	
		3 p.p.m. $MnSO_4$		
0.013	2	2.18	2.15	10.5
0.013	2	2.20	2.17	11.0
0.013	2	3.45	3.15	10.6
0.013	2	3.10	2.93	10.6
0.013	2	1.52	1.50	10.0
0.010	2	1.80	1.78	10.5
			$k_{o(ave)}$ = 10.6 x 10^{-4} moles/lit.hr.	

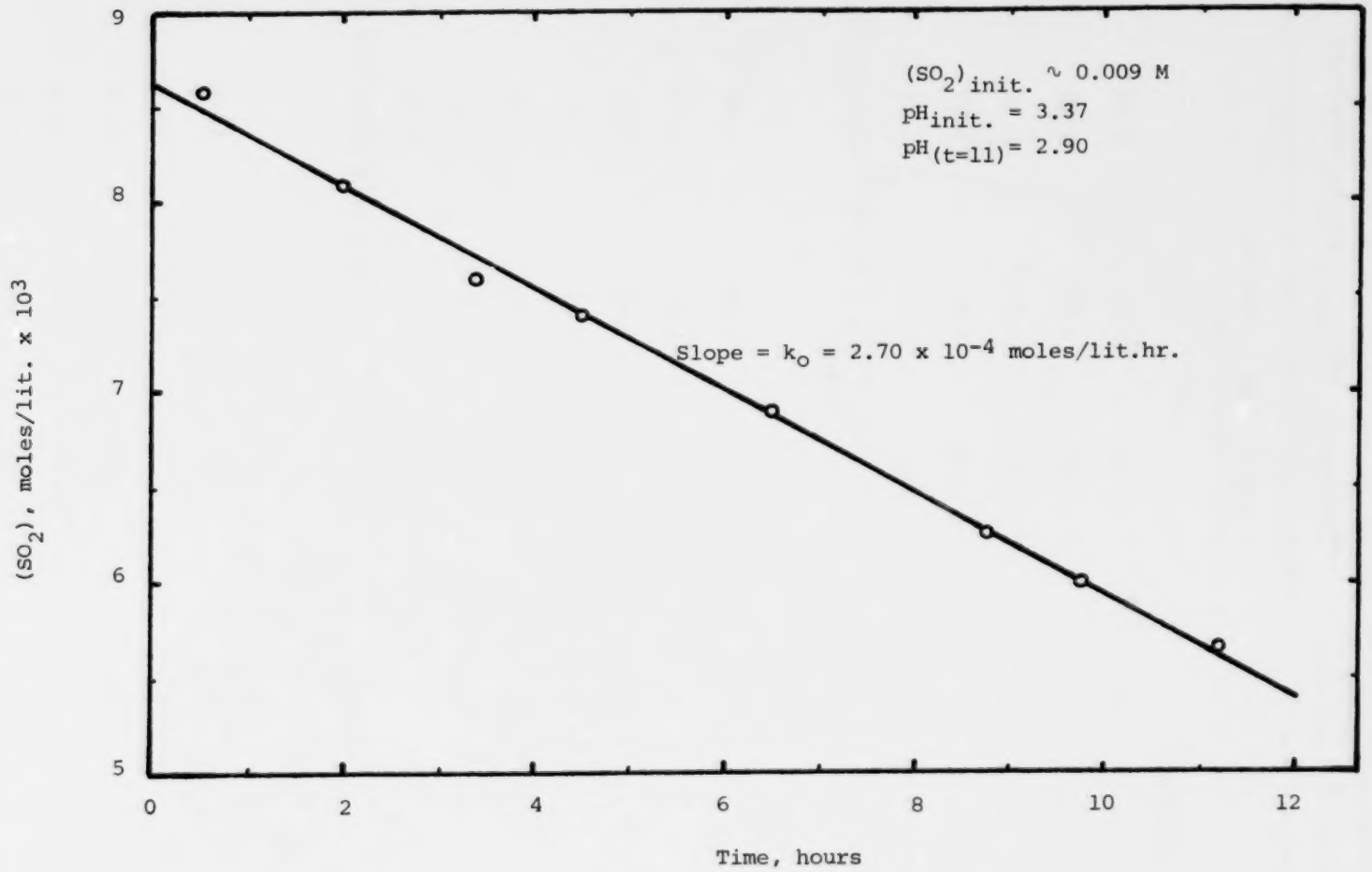


Fig. 9. SO_2 concentration as a function of time, with 1 p.p.m. $MnSO_4$ and $pH_{initial}$ of 3.4.

When the pH was raised above 4, the reaction rate was greatly increased in the first few moments, indicating that sulfite ion was present in solution. We can therefore conclude that the hydrogen ion concentration has an important influence on the rate of SO_2 oxidation when the pH of the solution is above 4 because it determines the relative amounts of bisulfite and sulfite present. However, when the pH is below 4, the hydrogen ion concentration does not affect the reaction in any way.

It is interesting to see how the ionic strength of our reacting solution was altered as we changed the initial pH. The ionic strength of our original solution (initial (SO_2) - 0.013 M, pH = 2.2) was 0.0065 moles/lit. while upon additon of NaOH to obtain a pH of 4, the ionic strength increased to about 0.01 moles/lit. According to the Debye-Hückel theory, the dependence of our zero-order reaction rate constant on the ionic strength of the solution of 25°C can be expressed as

$$\log \frac{k_{o(I)}}{k_{o(II)}} = 1.02\, Z_A Z_B \left(\sqrt{\mu_I} - \sqrt{\mu_{II}} \right) \qquad (7)$$

where $k_{o(I)}$ = zero-order reaction rate constant for ionic strength μ_I

$k_{o(II)}$ = zero-order reaction rate constant for ionic strength μ_{II}

Z_A, Z_B = valences of species involved in the reaction (see Laidler[30], pp. 220-221)

For the change of pH from 2.2 to 4 with our method, the change in ionic strength is too small to cause any significant change in the zero-order reaction rate constant, even if the absolute value of the product $Z_A Z_B$ were as large as 3.

However, when the pH of our solution was changed from 2.2 to 1 (by adding 25 ml. of 1 N HCl), the ionic strength changed from 0.0065 to 0.04 moles/lit. Theoretically, this change would cause a 25% change in k_o if the absolute value of the product $Z_A Z_B$ were 1, or a 63% change if the absolute value of $Z_A Z_B$ were 2. Large changes of k_o were not observed in our experiments, indicating a rather small influence of ionic strength on the reaction. However, it must be mentioned that the reliability of our results of pH values close to 1 is less than the reliability at pH values above 2 (there was a large scatter in data before the values for pH $\sim$ 1, shown in Table 1, were obtained). To get a clearer idea of the ionic strength influence on the rate of reaction, a larger change in ionic strength than in our experiments would have to be made. At any rate, the primary aim of this part of our investigation was not to study the ionic strength effects, but to find out whether the hydrogen ion is in any way involved in the reaction.

In the past, several researchers (Hoather & Goodeve[22] , Johnstone & Coughanowr[24] , Matteson et al.[32], Foster[14] , Gunn and Saleem[20]) have observed that increasing acidity slows down the SO_2 oxidation rate. However, in all these cases the pH of the solution was changed either by external addition of sulfuric acid or by the formation and accumulation of H_2SO_4 in the course of the oxidation reaction itself. Judging from our results, which show independence of the bisulfite oxidation rate on the hydrogen ion concentration, it it appears that it is the sulfate ion which affects the reaction rate in some manner. Our next series of experiments, therefore, dealt with the influence of externally added sulfate ions on the SO_2 oxidation rate at low pH.

Johnstone and Coughanowr[24] were the only authors who published detailed data on the retarding effect of H_2SO_4 addition on the reaction. The reaction rates went down as increasing amounts of sulfuric acid were added to the solution prior to the start of the oxidation, but the reaction remained zero order with respect to SO_2 concentration. The authors analyzed the initial apparent zero-order reaction rate as a function of H_2SO_4 concentration. Table 2 shows the results of their experiments, which were done with 12. 5 p.p.m. $MnSO_4$ and an initial SO_2 concentration of 0.002 M. Similar behavior was noticed by Hoather & Goodeve[22] (for 1 - 10 p.p.m. $MnSO_4$) and Gunn & Saleem[20] (for 1500 p.p.m. $MnSO_4$), but their results were not given in a clear form.

One of the most noteworthy conclusions which emerged from our experimental analysis dealing with sulfate effects is the fact that kinetic results can be conveniently presented using the ratio $(SO_4^=)_{added}/(SO_2)_{initial}$. When Johnstone and Coughanowr's kinetic data from Table 2 are plotted as a function of this new variable, the graph shown in Fig. 10 is obtained.

The source of sulfate ions in our experiments was sodium sulfate. Addition of Na_2SO_4 prior to the start of the reaction slowed the oxidation rate considerably. However, for all amounts of Na_2SO_4 that were added, the initial reaction rate remained zero order. (By initial reaction rate we mean the rate observed until at least 30% of the originally present SO_2 had reacted.) Fig. 11 and Fig. 12 show the dependence of the zero-order reaction rate constant, k_o, on the ratio $(SO_4^=)_{added}/(SO_2)_{initial}$ for the cases where the catalyst concentrations were 1 and 3 p.p.m. In both instances, the initial SO_2 concentration was around 0.013 M. Two representative runs from these series of experiments are presented in Fig. 13 and Fig. 14. Now, Table 3 lists the zero-order reaction rate constants obtained for various initial SO_2 concentrations, catalyst concentrations, and $(SO_4^=)_{added}/(SO_2)_{initial}$ ratios. The initial pH is given for all of our work, but is not available for Johnstone & Coughanowr's data. The zero-order reaction rate constants shown in Table 3 are actually the average values calculated from several series of runs. The actual values obtained in experiments are shown in Table 4.

From Table 3, the ratios k_o(with sulfate added)/k_o(without any sulfate added) can be formed for each column (see Table 5). From the trend of these ratios with increasing values of $(SO_4^=)_{added}/(SO_2)_{initial}$, it is possible

TABLE 2. Results of Johnstone and Coughanowr[24]

$(SO_2)_{initial}$ = 0.002 M

$(O_2)_{initial}$ = 0.0003 - 0.007 M

12.5 p.p.m. $MnSO_4$

Initial H_2SO_4 (added), M	k_o, moles/lit.hr. x 10^3
0	12.10
0.002	4.20
0.02	1.65
0.035	1.08
0.05	0.42
0.1	0.30

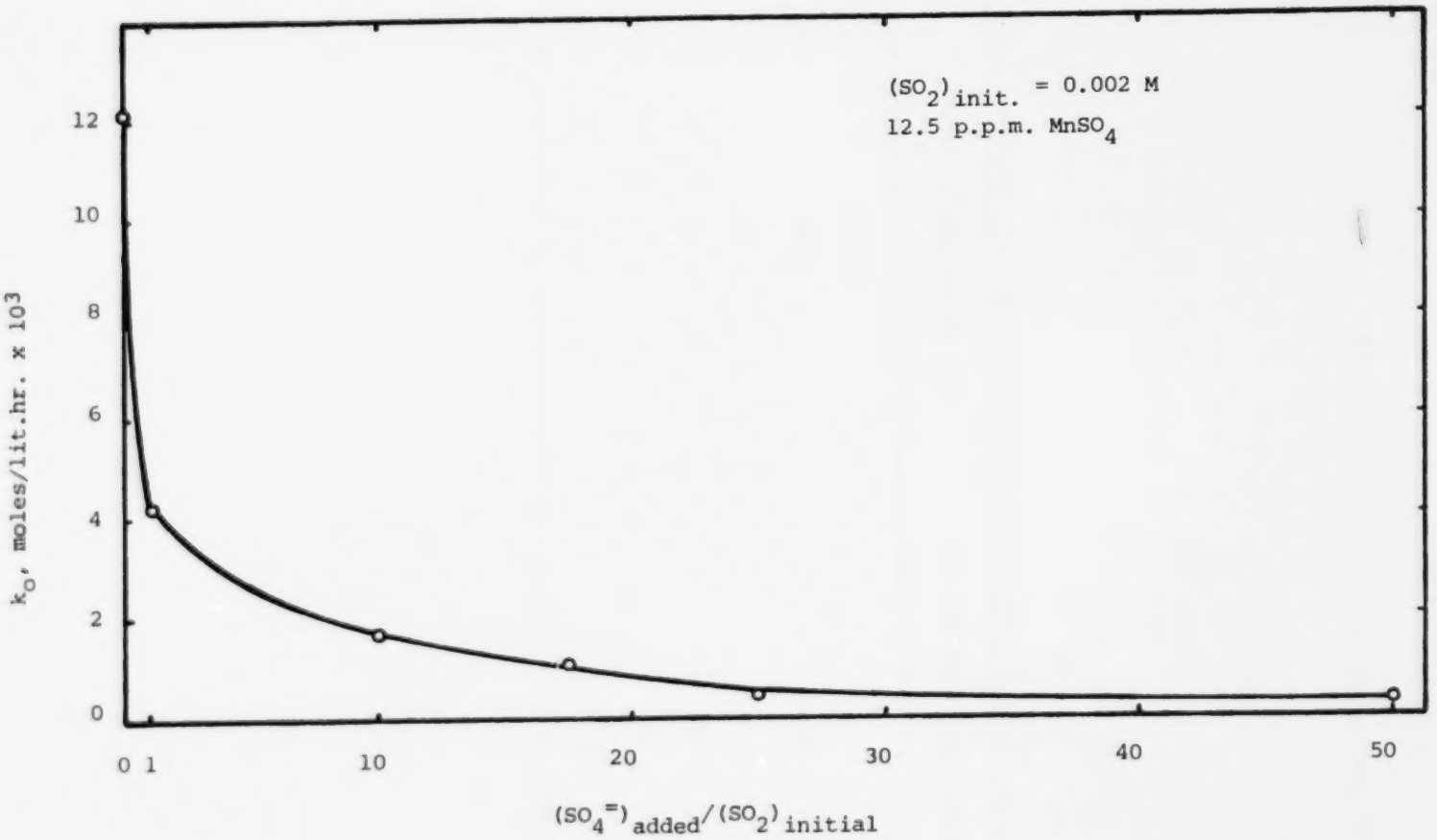


Fig. 10. Zero-order reaction rate constant, k_o, as a function of $(SO_4^{=})_{added}/(SO_2)_{initial}$ from Johnstone & Coughanowr's[24] data.

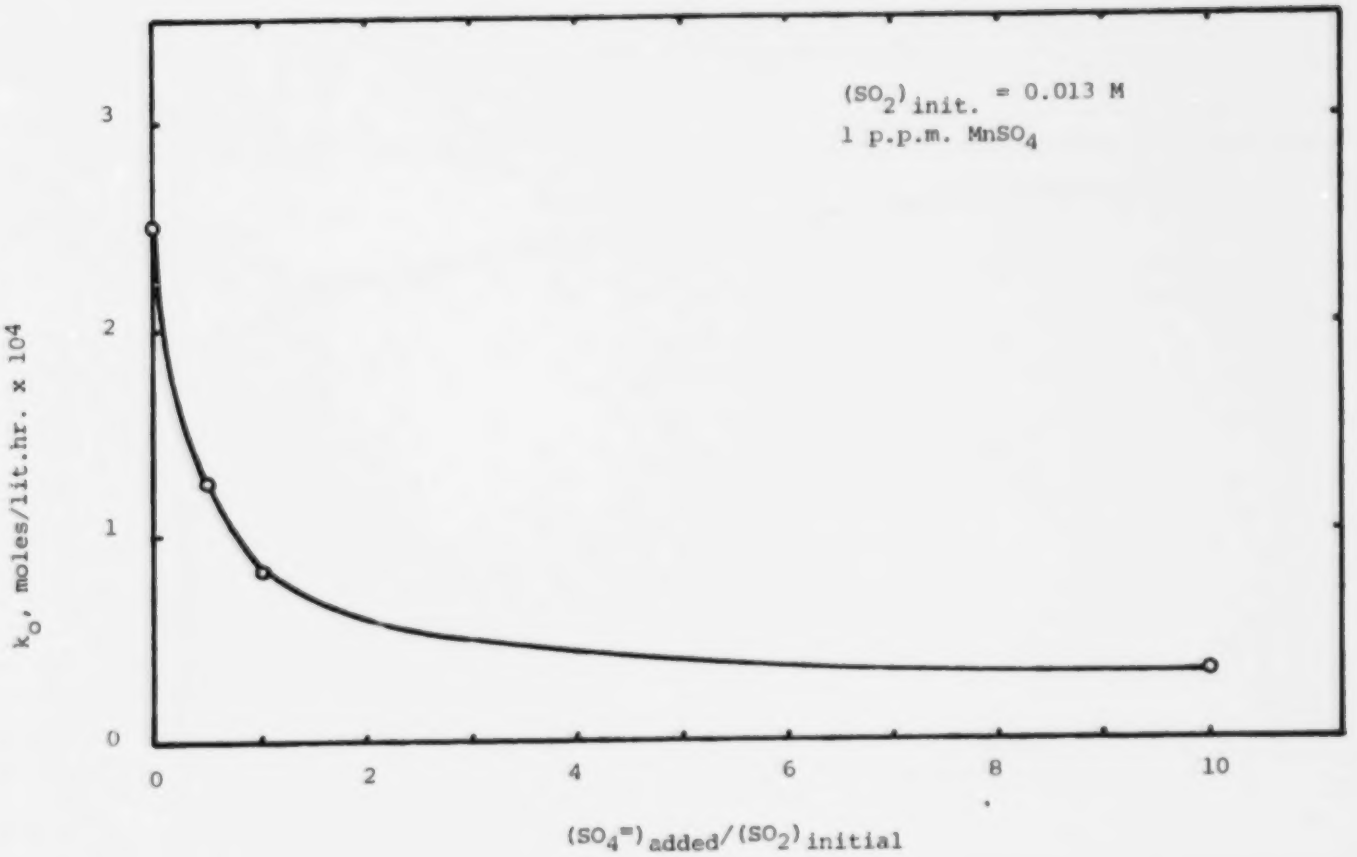


Fig. 11. Zero-order reaction rate constant, k_o, as a function of $(SO_4)_{added}/(SO_2)_{initial}$, with 1 p.p.m. $MnSO_4$ catalyst.

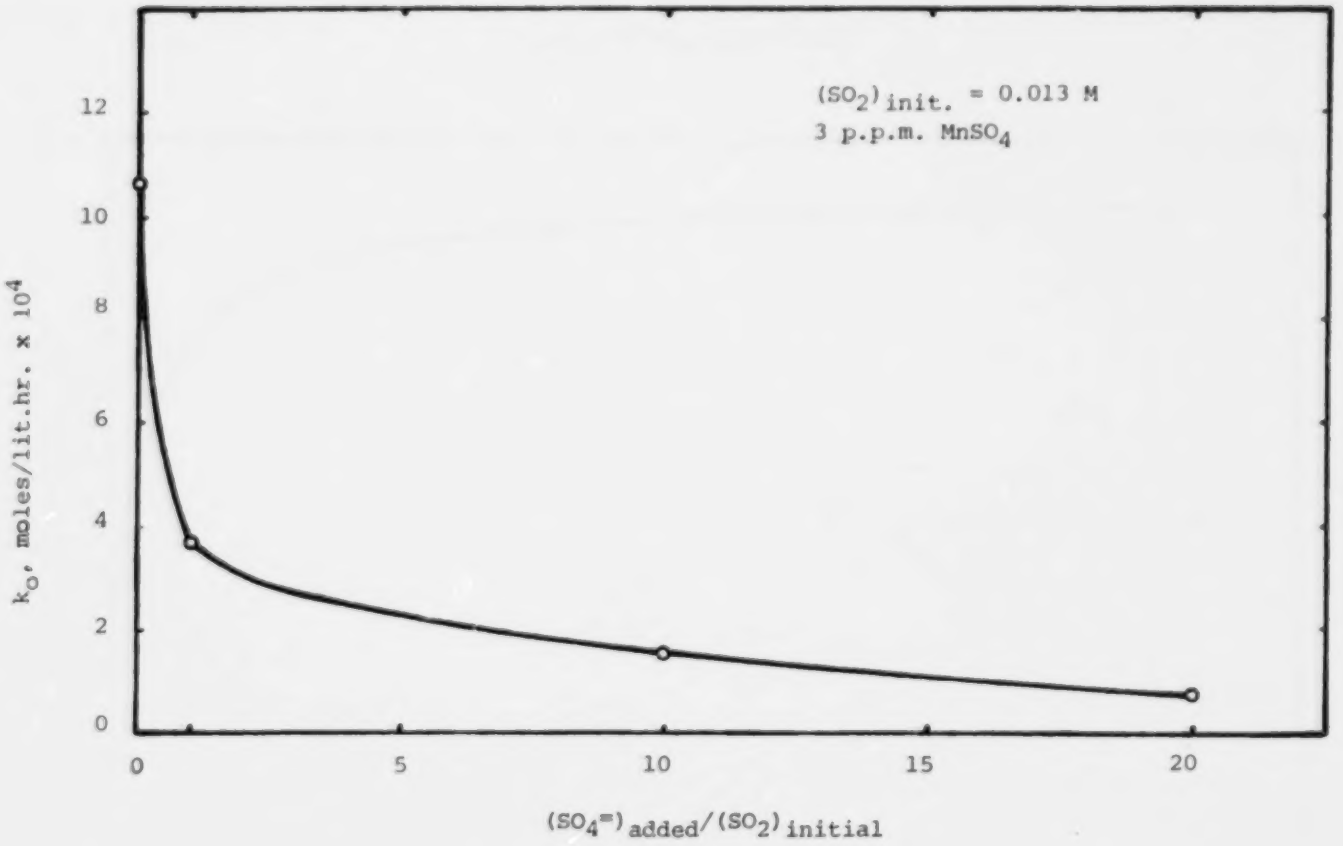


Fig. 12. Zero-order reaction rate constant, k_o, as a function of $(SO_4^{=})_{added}/(SO_2)_{initial}$, with 3 p.p.m. $MnSO_4$ catalyst.

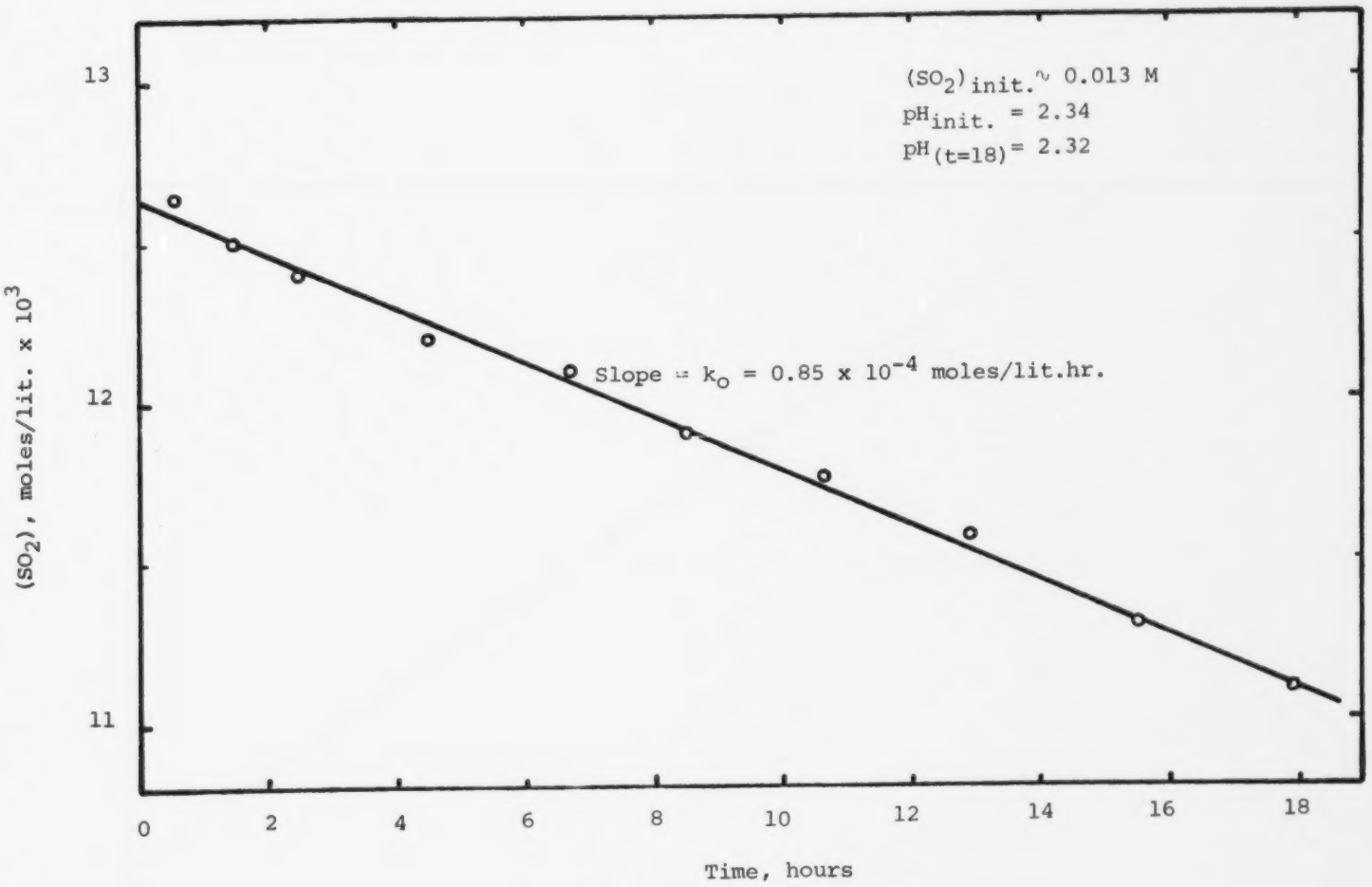


Fig. 13. SO_2 concentration as a function of time, with 1 p.p.m. $MnSO_4$ catalyst and $(SO_4^{=})_{added}/(SO_2)_{initial} = 1$.

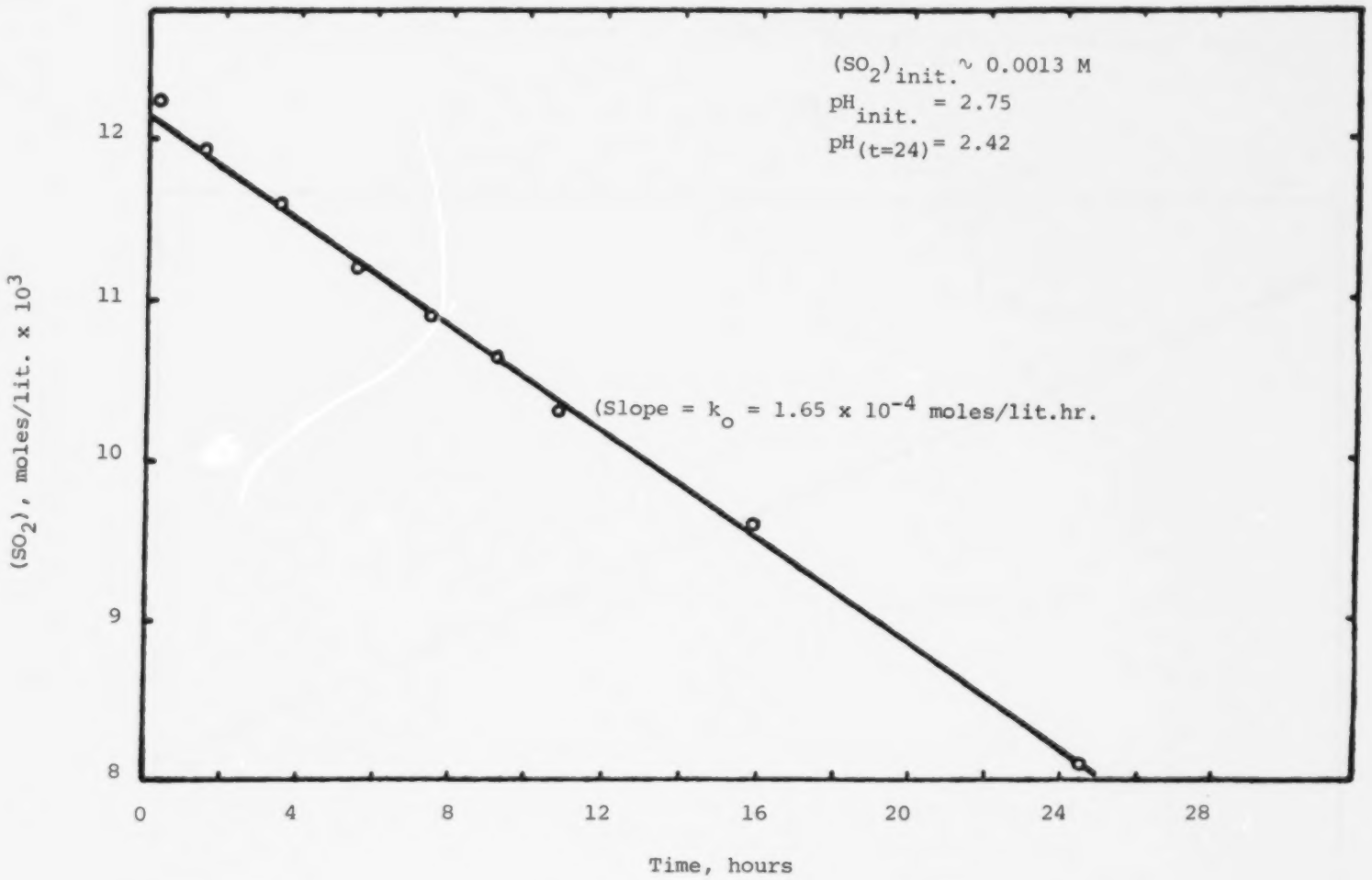


Fig. 14. SO_2 concentration as a function of time, with 3 p.p.m. $MnSO_4$ catalyst and $(SO_4^{=})_{added}/(SO_2)_{initial} = 10$.

Table 3. Zero-order reaction rate constants for different experimental conditions.

Units of k_o: moles/lit.hr.

$\frac{(SO_4^=)_{added}}{(SO_2)_{initial}}$	12.5 p.p.m. $MnSO_4$ $(SO_2)_{init.}$ = 0.002 M (Johnstone & Coughanowr[24])	1 p.p.m. $MnSO_4$ $(SO_2)_{init.}$ = 0.013 M	3 p.p.m. $MnSO_4$ $(SO_2)_{init.}$ = 0.013 M	3 p.p.m. $MnSO_4$ $(S)_2)_{init.}$ = 0.08 M
0	$k_o = 12.1 \times 10^{-3}$	$k_o = 2.5 \times 10^{-4}$	($pH_{init.}$ = 2.17)	($pH_{init.}$ = 1.60)
0.5	$k_o = 5.8 \times 10^{-3}$	$k_o = 1.24 \times 10^{-4}$ ($pH_{init.}$ = 2.30)		
1	$k_o = 4.2 \times 10^{-3}$	$k_o = 0.84 \times 10^{-4}$ ($pH_{init.}$ = 2.32)	$k_o = 3.63 \times 10^{-4}$ ($pH_{init.}$ = 2.25)	$k_o = 3.7 \times 10^{-4}$ ($pH_{init.}$ = 1.80)
10	$k_o = 1.65 \times 10^{-3}$	$k_o = 0.34 \times 10^{-4}$ ($pH_{init.}$ = 2.75)	$k_o = 1.55 \times 10^{-4}$ ($pH_{init.}$ = 2.80)	
20	$k_o = 0.75 \times 10^{-3}$		$k_o = 0.75 \times 10^{-4}$ ($pH_{init.}$ = 2.90)	

TABLE 4. RESULTS OF KINETIC EXPERIMENTS DEALING WITH SULFATE EFFECTS

$(SO_4^{=})_{added}/(SO_2)_{initial}$	Length of run (hr)	$pH_{initial}$	k_o, moles/lit.hr. x 10^4
1 p.p.m. $MnSO_4$, $(SO_2)_{initial}$ = 0.013 M			
0	S E E	T A B L E	1
0.51	23	2.28	1.20
0.54	23	2.30	1.32
0.54	15	2.32	1.30
0.54	24	2.30	1.20
0.99	10	2.31	0.82
0.95	13	2.31	0.83
0.95	14	2.29	0.81
1.00	20	2.34	0.85
10.00	24	2.75	0.33
10.25	24	2.75	0.37
3 p.p.m. $MnSO_4$, $(SO_2)_{initial}$ = 0.013 M			
0	2	2.17	11.1
0	2	2.17	10.2
0	2	2.16	9.7
0	2	2.16	11.0
0	2	2.18	10.5
0	2	2.15	10.3
1.04	7	2.26	3.7

TABLE 4 (continued)

$(SO_4^{=})_{added}/(SO_2)_{initial}$	Length of run (hr)	$pH_{initial}$	k_o, moles/lit.hr.x 10^4
3 p.p.m. $MnSO_4$, $(SO_2)_{initial}$ = 0.013 M (cont'd)			
1.06	7	2.26	3.7
1.05	8	2.21	3.5
1.06	8	2.23	3.5
1.10	6	2.25	3.65
1.00	7	2.20	3.7
10.10	24	2.80	1.5
10.05	24	2.80	1.6
10.00	24	2.75	1.65
10.10	24	2.78	1.55
20.00	20	2.83	0.74
21.00	20	2.90	0.75
3 p.p.m. $MnSO_4$, $(SO_2)_{initial}$ = 0.080 M			
0	2	1.60	11.1
0	2	1.60	10.7
1.00	7	1.80	3.7
1.05	7	1.80	3.8

TABLE 5. RATIOS OF k_o (WITH SULFATE ADDED)/k_o(WITHOUT SULFATE ADDED) FOR VARIOUS EXPERIMENTAL CONDITIONS

$\frac{k_o(\text{sulfate added})}{k_o(\text{without sulfate added})}$	12.5 p.p.m. $MnSO_4$ $(SO_2)_{init.}$=0.002 M	1 p.p.m. $MnSO_4$ $(SO_2)_{init.}$=0.013 M	3 p.p.m. $MnSO_4$ $(SO_2)_{init.}$=0.013 M	3 p.p.m. $MnSO_4$ $(SO_2)_{init.}$=0.08 M
$\frac{k_o(SO_4^{=}/SO_2 = 0)}{k_o(SO_4^{=}/SO_2 = 0)}$	1.00	1.00	1.00	1.00
$\frac{k_o(SO_4^{=}/SO_2 = 0.5)}{k_o(SO_4^{=}/SO_2 = 0)}$	0.48	0.50		
$\frac{k_o(SO_4^{=}/SO_2 = 1)}{k_o(SO_4^{=}/SO_2 = 0)}$	0.35	0.34	0.34	0.34
$\frac{k_o(SO_4^{=}/SO_2 = 10)}{k_o(SO_4^{=}/SO_2 = 0)}$	0.14	0.14	0.15	
$\frac{k_o(SO_4^{=}/SO_2 = 20)}{k_o(SO_4^{=}/SO_2 = 0)}$	0.6		0.07	

to infer that the reaction is decreased proportionally in each column. This is the basis for combining the results into a dimensionless diagram (Fig. 15), showing the dependence of the ratio k_o(with sulfate added)/k_o(without any sulfate added) on the ratio $(SO_4^{=})_{added}/(SO_2)_{initial}$ is an extremely important kinetic index of the SO_2 oxidation rate. No matter what the initial SO_2 concentration and the catalyst concentration are, at a certain value of this ratio, the reaction rate is always slowed down to the same extent. This particular characteristic of SO_2 oxidation kinetics at low pH has not been reported before.

It is interesting to note that Johnstone & Coughanowr's data fit in very well with ours, although their source of sulfate ions was sulfuric acid. This fact seems to confirm the independence of the SO_2 oxidation rate on the hydrogen ion concentration at low pH values, which we observed in earlier experiments. Therefore, in the present SO_2 system, the sulfate ion is the only species responsible for retarding the reaction.

The experiments described above were performed with sulfate that was externally added to the SO_2 solution. It must be remembered, though, that sulfate is also produced in the course of the SO_2 oxidation itself. Hoather & Goodeve[22] and Johnstone & Coughanowr[24] observed that, for unexplained reasons, the acid formed by the reaction did not slow the oxidation down. However, they used a limited amount of oxygen and could not follow the reaction to any great extent. With our stystem of continuous oxygen supply, we could follow the reaction until practically all of SO_2 had reacted. Nevertheless, the "internally produced" sulfate does not appear to affect the reaction rate significantly. In some of our runs, a slight retarding effect could be noticed after the reaction was allowed to proceed for more than 25 hours (see Fig. 16). Even when observed, the effect was much smaller than would be expected from the generalized diagram of Fig. 15. This relative lack of influence of the "internally produced" acid is rather puzzling. Foster's[14] theory that, at the low concentrations of $MnSO_4$ and H_2SO_4 used by Hoather & Goodeve and Johnstone & Coughanowr, the complexing reaction between them takes place so slowly that very little complexing occurs in the time of the experiment, does not appear fully adequate since sulfate concentrations did reach significant levels in the course of our reaction (up to 0.01 M). It is true that in all cases examined, the manganese concentration was very low — it did not exceed 12.5 p.p.m. (8.2×10^{-5} M).

An attempt at explaining the shape of graphs in Fig. 11 and Fig. 12 could include the effect of the decreasing oxygen solubility with increasing ionic strength on the reaction rate constant. It could be assumed that the reaction rate constant, k_o, can be written as $k_o = k\,(O_2)^n$, where k is some constant and n is the unknown order of reaction with respect to oxygen. As more sulfate is added, the oxygen concentration might be decreasing due to increased ionic strength. Bassett and Parker[5] observed an effect of this kind as they added large amounts of HCl to their reacting solution; the reaction rate was affected for HCl concentrations above 0.1 N. Also, the changing ionic strength, due to the addition of sulfate, might be reducing the reaction rate constant according to the Debye-Huckel theory (see equation (7)).

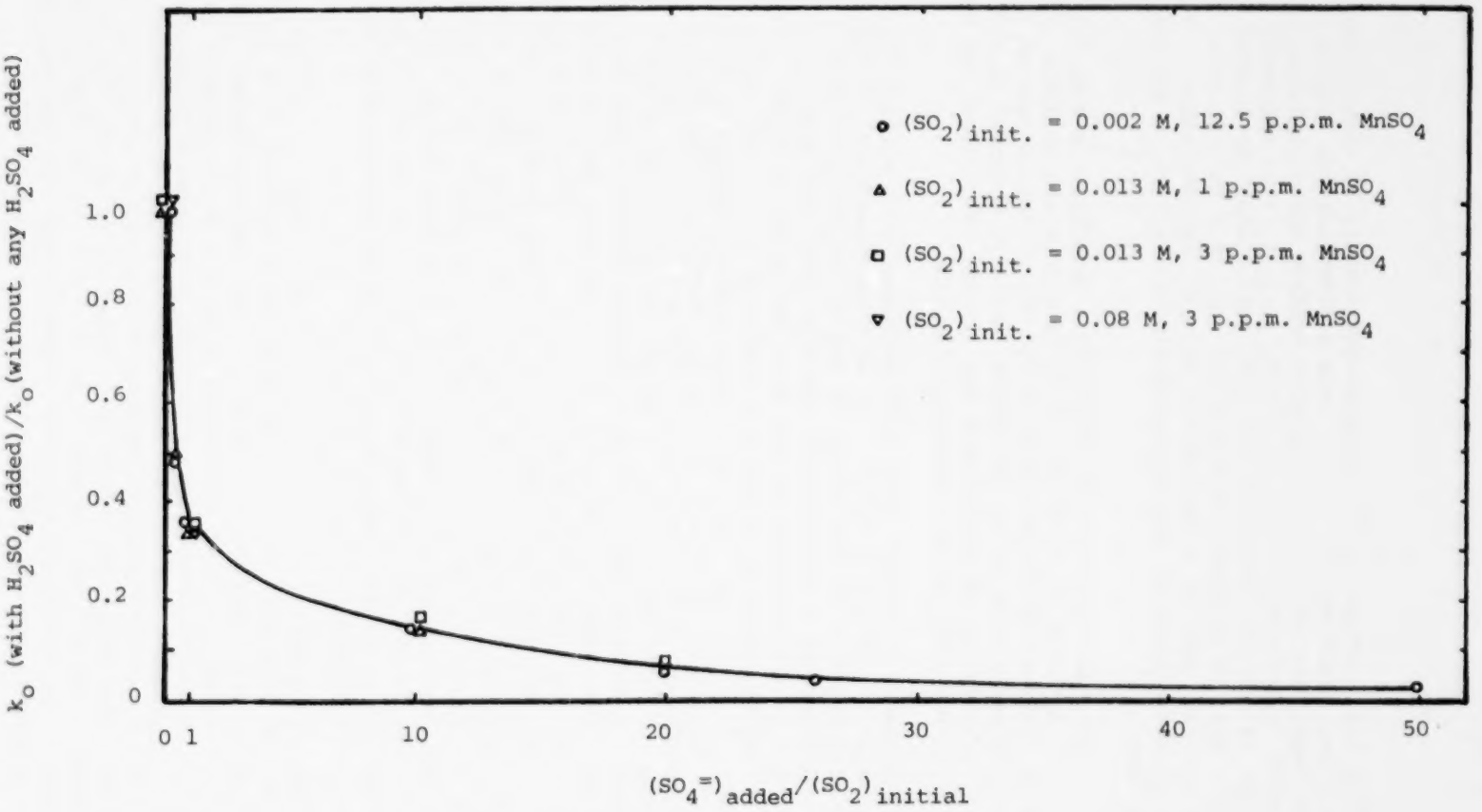


Fig. 15. Dimensionless diagram of k_o(with sulfate added)/k_o(without any sulfate added) as a function of $(SO_4^{=})_{added}/(SO_2)_{initial}$.

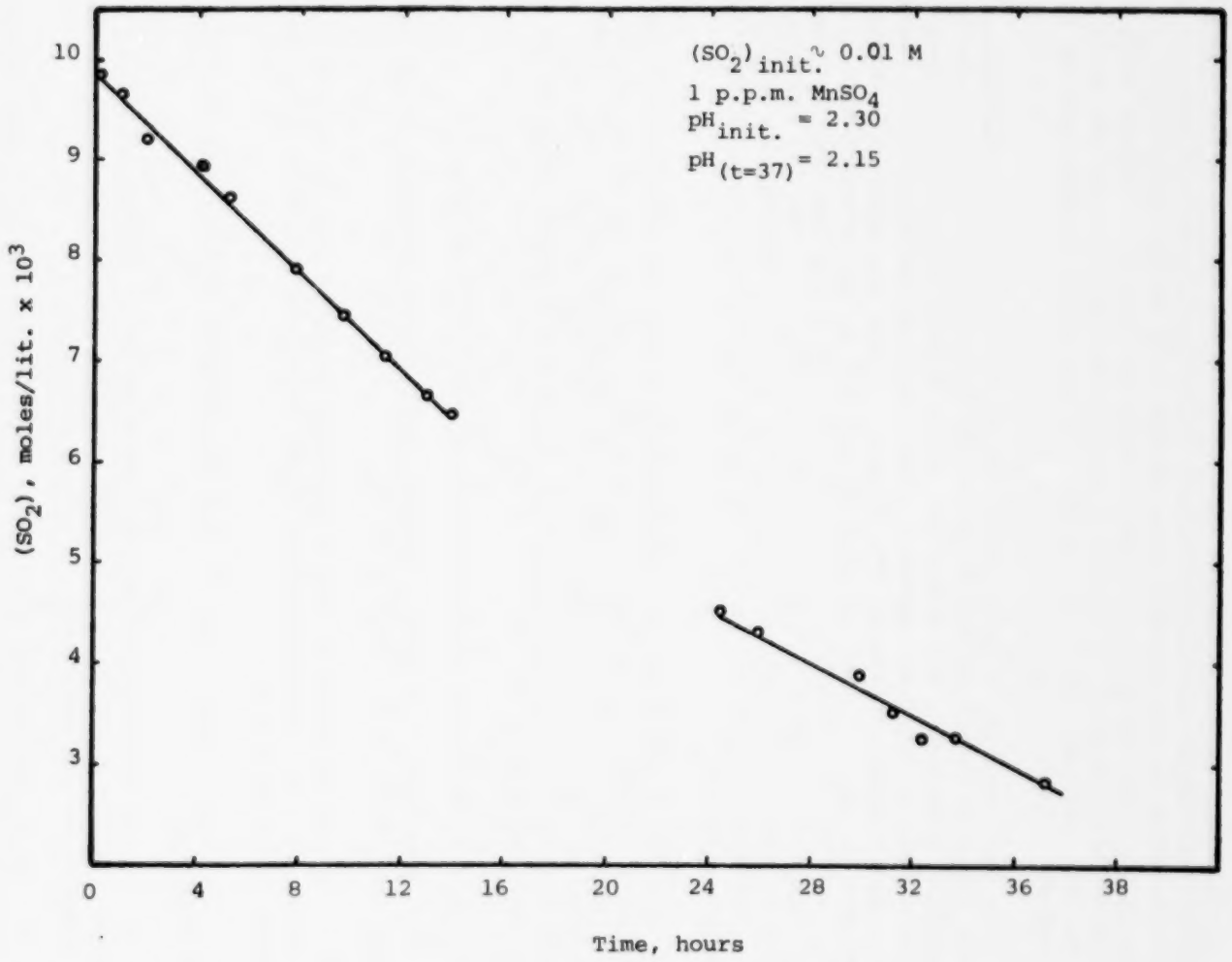


Fig. 16. Effect of the "internally produced" sulfate.

However, the dimensionless graph on Fig. 15, which is independent of the initial SO_2 concentration and the concentration of $SO_4^=$ added, seems to indicate that oxygen solubility effects cannot account for the observed behavior. The retardation of the reaction rate depends only on the ratio $(SO_4)_{added}/(SO_2)_{initial}$, and not on the absolute concentrations of the added sulfate (which varied from 0.001 M to 0.26 M), and, therefore, not on the ionic strength. We can then conclude that oxygen solubility and ionic strength effects do not appear to be significant in our system.

The fact that SO_2 oxidation rate is zero order in SO_2 concentration and second order in manganese (the latter observed by Johnstone and Coughanowr[24] Coughanowr & Krause[10], and Walter[52]), while inhibited by sulfate, seems to indicate that an important factor in the kinetic mechanism is the formation of a complex between manganese and sulfate. Since the order with respect to manganese is two, the catalyst must be involved in the rate-determining step. It is possible that manganese in the +3 state is formed and that it complexes with sulfate. It appears from dimensionless diagram in Fig. 15 that the complexing reaction, either with sulfate or bisulfite, or both, involves an equilibrium since the same portion of catalyst is always tied up at a certain $(SO_4^=)_{added}/(SO_2)_{initial}$ ratio.

In order to get a better understanding of the rate-determining step and the kinetic mechanism that might be involved in SO_2 oxidation at low pH, the oxygen order of the reaction should be determined and a closer study of the influence of the ionic strength on the rate of reaction should be made. A better idea of the species involved in the rate-determining step of the reaction would then be gained.

The results of our experiments can be summarized as follows:

1. Both $MgSO_4$ and $MnSO_4$ catalyzed liquid-phase oxidation of SO_2 at low pH are zero order in SO_2 concentration.

2. While manganese is a very effective catalyst even at concentrations as low as 3 p.p.m., magnesium shows little catalytic action at concentrations as high as 20,000 p.p.m.

3. Energy of activation for the Mn-catalyzed reaction was found to be 18.7 kcal/mole.

4. Low pH oxidation of SO_2, catalyzed by $MnSO_4$, is independent of pH between 1 and 4, while at pH values above 4 the reaction speeds up due to the presence of sulfite ions.

5. Ionic strength did not appear to affect the reaction rate significantly, but additional experiments at higher ionic strengths should be performed to check this effect.

6. Sulfate ions inhibit the reaction significantly.

7. Kinetic results can be presented conveniently using the ratio $(SO_4^{=})_{added}/(SO_2)_{initial}$.

8. Dimensionless diagram of ratio k_o(with sulfate added)/k_o(without any sulfate added) vs. ratio $(SO_4^{=})_{added}/(SO_2)_{initial}$ was obtained for a range of SO_2 concentrations from 0.002 to 0.08 M and $MnSO_4$ catalyst concentrations from 1 to 12.5 p.p.m.

9. The mechanism of the reaction seems to involve complexing of Mn with $SO_4^{=}$, but further work is necessary to make definite conclusions.

IV. HIGH pH UNCATALYZED OXIDATION OF SULFUR DIOXIDE

The uncatalyzed SO_2 oxidation at high pH values is extremely important in the atmospheric chemistry of sulful dioxide, particularly for its oxidation in drops with NH_3 present. Also, since most industrial SO_2 scrubbers work at higher pH, the oxidation rate is significant in demonstrating how rapid the SO_2 oxidation at high pH is, even without the presence of catalyst.

As the pH of a solution containing SO_2 rises, $SO_3^=$ becomes the predominant species; therefore, by high pH SO_2 oxidation we primarily mean sulfite oxidation. If the pH is above 9, all of SO_2 is in $SO_3^=$ form (the equilibrium constants being $K_1 = 1.74 \times 10^{-2}$, $K_2 = 6.24 \times 10^{-8}$) (Fig. 1).

Literature

The most extensive work on uncatalyzed sulfite oxidation was done by Fuller and Crist[16] in 1941. They were the first to show that the oxidation of sulfite could occur in the absence of metals. The essential parts of their apparatus were a quartz reaction vessel in which a weighed amount of Na_2SO_3 and 40 ml. of water were placed, a gas buret for the direct measurement of the rate of oxygen absorption, and a thermostat (the temperature was 25°C). The amount of oxygen absorbed during a run, together with the iodine titer at the end, was used to calculate the sulfite concentration present at t_o. Fuller and Crist went through extreme care in purifying all reactants involved, distilling the water in a special way to make certain that no heavy metals came over. Their results show a first order reaction in sulfite, with the reaction rate constant, k_1, having a value of 0.013 sec^{-1}. They worked with the oxygen pressure of 1 atm. Initial sulfite concentrations ranged from 0.01 to 0.05 M, and the pH of the solution was in the range 8.2 - 8.8. However, the authors indicate that at sulfite concentrations above 0.015 M, the reaction was affected by the rate of oxygen transfer to the solution at their maximum practical stirrer speed of 1600 r.p.m. Considering that they used a value of 5×10^{-6} for the second dissociation constant of SO^2, which is two orders of magnitude off the correct value, some question arises over their results. Taking the correct value for K_2, there is about 15% less sulfite at pH = 8.2 than Fuller and Crist assumed (see Fig. 1). Only when pH is above about 8.9 is all of SO_2 converted to the $SO_3^=$ form.

In spite of some deficiencies, the work of Fuller and Crist is far more reliable than that of other workers before them (Bäckström[3], Reinders et al.[41], Tittoff[49]) due to the purity of the substances used. The reaction is

Preceding page blank

extremely sensitive to the presence of metal ions; some catalysts (primarily copper) affect the rate even at concentrations as low as 10^{-8} M[16].

It must be pointed out that Fuller and Crist's[16] constant k_1 includes in it the oxygen concentration since the amount of dissolved oxygen remained more or less constant in the course of the reaction. At P_{O2} = 1 atm., solubilities of oxygen in sulfite solutions of various concentrations are given by Linek and Mayrhoferova[31]. For $(SO_3^=)$ = 0.02 M, this solubility is around 0.0013 M, which is close to the oxygen solubility in water given in Perry's Handbook[37] as 0.00123 M. The order of reaction with respect to oxygen was not determined by Fuller and Crist.

Recent kinetic investigations do little to clarify the reaction kinetics or mechanism. Barron and O'Hern[4] used a rapid-mixing method to eliminate the mass transfer of oxygen to the solution. Their tube-reactor was made of plastic. Sulfite concentrations ranged from 0.05 M to 0.05 M, while the oxygen pressure was 3.44×10^5 pa. The temperature was 25°C. They concluded that the oxidation rate is proportional to three-halves power in sulfite and independent of the oxygen concentration:

$$r = k_e \quad (SO_3^=)^{3/2} \tag{8}$$

with $k_e = 0.065\ (l)^{\frac{1}{2}}/(gmole)^{\frac{1}{2}}(sec)$. Barron and O'Hern used deionized water, but had copper impurities present on the order of 10^{-7} M.

Yagi and Inoue[56] studied sulfite oxidation using a polarographic method. They used distilled water, but did not de-ionize it. Sulfite concentrations ranged from 0.001 to 0.08 M. Their rate equation at 20°C is

$$r = 1.4\ (SO_3^=) \cdot (O_2) \quad gmol/lit.sec., \tag{9}$$

giving a first-order dependence on oxygen concentration.

Srivastava, McMillan and Harris[47] also found that the reaction rate is first order with respect to the oxygen concentration. Their sulfite concentration was above 0.04 M, while the oxygen concentration in solution ranged from 0.0006 to 0.0024 M. Temperature was set at 20°C. They used Barron and O'Hern's[4] technique. However, the authors themselves admit that they had copper impurities on the order of 3×10^{-6} M, a concentration which would have a marked effect on the reaction rate.

Winkelmann[55] found the reaction rate independent of oxygen concentration.

Obviously, there are uncertainties regarding the order of oxygen for the uncatalyzed reaction rate. As far as the actual kinetic results are concerned, Fuller and Crist's[16] findings seem to be more reliable than others due to high purity of their reactants; however, the controversy of kinetic expressions requires a check of their results.

Experimental Apparatus and Procedure

In a work closely associated with ours, Ness[35] tried to check the results of Fuller and Crist[16], primarily having in mind the fact that they did not measure the activation energy of the uncatalyzed reaction and therefore could have been mass-transfer controlled in their experiments. However, Ness' results indicated that the oxygen transfer to the sulfite solution was the controlling factor in his experiments. The sulfite oxidation rate was constant with time and the energy of activation was virtually zero.

Our apparatus was similar to that used by Ness; however, certain modifications were made to insure operation which would yield purely kinetic data instead of being controlled by mass transfer of oxygen to the solution. The apparatus resembled the one used in our work with the catalyzed SO_2 oxidation at low pH, except that now the reactor was a three-neck, 1-liter quartz flask (see Fig. 17).

Ness used an initial solution volume of 500 ml. and continuously took samples through the sample tube to follow the change in sulfite concentration with time. His stirring speed was around 500 r.p.m.

In our experiments, we used a reacting volume of 50 ml., and a stirrer speed of over 1500 r.p.m., which brought about a large change in the surface area for oxygen absorption; as a result, mass transfer rate was increased manyfold over the one obtained by Ness.

The reaction rate was so rapid that it was impossible to continuously take samples without introducing a large error. Also, the volume of the solution in the reactor was so small that sample taking would have been difficult. Therefore, the reaction was quenched with iodine directly in the reactor after desired period of time. One run in the reactor gave only one data point. For different reaction times the procedure had to be repeated.

For the above reason, the neck used for the sample tube and valve in Ness' procedure (and in our low pH work) was now fitted with a 25-ml. teflon-stoppered burette with a pressure equalizing side-arm, which was used to supply the necessary iodine for quenching. The other burette, just as in Ness' work, was used to supply the sulfite necessary for the reaction.

Before each run, the reactor and attachments were cleaned with a concentrated potassium dichromate (H_2SO_4 + $K_2Mn_2O_7$) cleaning solution and rinsed many times with deionized water.

The reactor was filled with 40 ml. of deionized water to which an appropriate number of drops of HaOH were added in order to raise the pH above 10, the stirring bar was placed in it, and the fittings were attached to the flask necks. A Tygon tube leading from the oxygen supply was attached to the oxygen inlet. The joints were sealed with teflon sleeves. The assembly was placed in the constant temperature bath; all experiments

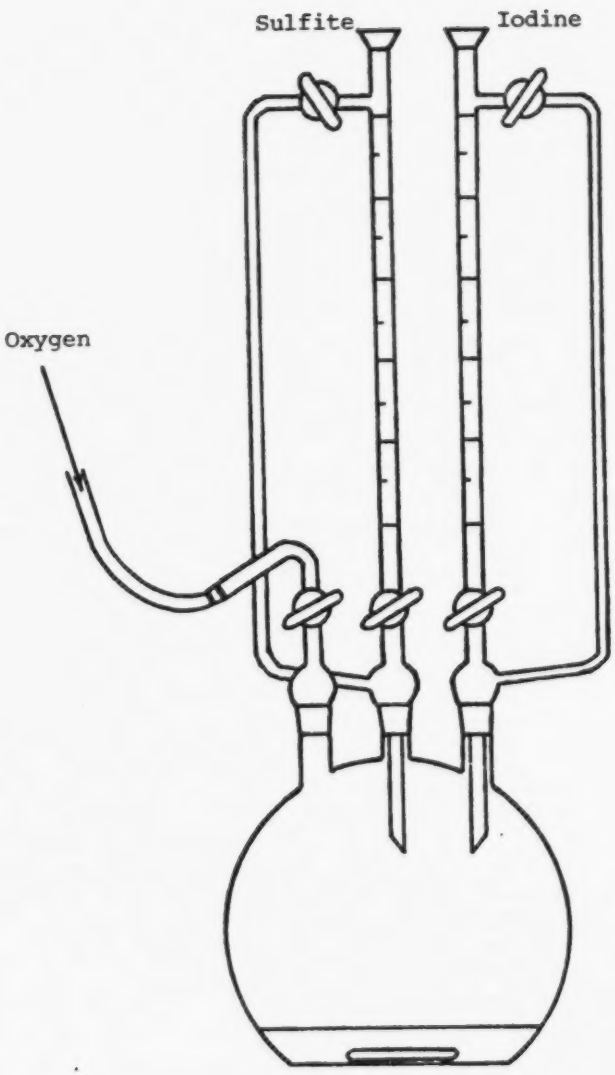


Fig. 17. Reactor for high pH uncatalyzed oxidation of sulfur dioxide.

were conducted at 25°C. Oxygen was blown through the reactor for several minutes to purge the air. The pressure was then set at 800 mm mercury, the magnetic stirrer was set on, and at least two hours were allowed for oxygen absorption.

The reaction started when 10 ml. of sodium sulfite solution were added to the volume in the flask through one of the burettes. The initial sulfite concentration in the reactor was close to 0.01 M. This was attained by weighing out 0.0650 g. of Na_2SO_3 and dissolving it in 10 ml. of deionized water. Na_2SO_3 and NaOH were used in the experiments since it was shown by several workers that sodium does not catalyze SO_2 oxidation[5,25,28].

To start the reaction, the oxygen supply was temporarily shut off, the stopcock on the pressure equalizing arm of the burette was opened, followed by the burette stopcock, thus adding the sulfite solution to the 40 ml. of solution already in the reactor. Both stopcocks were then shut and the oxygen pressure again adjusted to 800 mm Hg. Stirrer speed was increased to 1500 r.p.m. before the start of the reaction.

After the desired reacting time had elapsed, the reaction was quenched by introducing 15 ml. of 0.1 N iodine through the other burette. At the moment that quenching began, stirring speed was increased to a maximum of 1850 r.p.m., causing extreme violent stirring and splattering, so that iodine could quench the reaction even in drops on walls of the reaction flask. Iodine remaining on burette walls was washed down with 5 ml. of deionized water.

After the addition of iodine, 10 ml. of the resulting solution in the flask was withdrawn with a pipette and backtitration with 0.1 N arsenious acid was performed to determine the sulfite concentration at the time the reaction was quenched. To obtain the sulfite concentration at some other time, the apparatus was cleaned carefully in the manner already described and the procedure repeated. A sample calculation of the sulfite concentration is shown in Appendix B.

To determine the pH of the reacting solution, a separate series of runs was performed. The burette for iodine addition was replaced by the sample-taking tube and valve. At the desired time, a smaple was withdrawn and its pH measured as rapidly as possible.

Before the actual kinetic results for the uncatalyzed reaction are presented, the methods used in preparing the various solutions and the care taken in insuring their greatest possible purity under the given conditions should be described.

To obtain water that contained no traces of metal ions, regular deionized water from Roger Adams Laboratory supply was passed at rates of under 1.0 lit./hr through a quartz ion exchange column which held 0.45 kg of a cation-anion mixed bed exchange resin (Ag 501 - X 80), obtained from

BioRad, Inc. This column was capable of producing water whose specific resistance was in excess of 1.5 million ohm-cm. At the end of all our experiments, we found the specific resistance to be around 800,000 ohm-cm, which indicates excellent purity of the water used.

The pH of the deionized water was raised by adding drops of 1 N NaOH to it. 1 N NaOH was prepared from sodium hydroxide electrolytic pellets obtained from Fisher Scientific Company. Their certificate of actual lot analysis shows that there is a maximum 0.0002% of both iron and copper in the pellets. The calculation of iron and copper impurities in our reacting solution is done in Appendix C; there will be more comments about impurities later on in the text.

To prepare a reacting solution of pH 11.1, 0.84 ml. of 1 N NaOH was added to 300 ml. of deionized water. Forty ml. of this solution were placed in the quartz flask prior to the start of the reaction. Upon addition of Na_2SO_3, the pH was 11.1.

In order to keep the 1 N NaOH solution free of metal ions, it was placed in a special quartz container.

The Na_2SO_3 used was anhydrous sodium sulfite made by Fisher Scientific Company. The certificate of actual lot analysis shows a maximum of 0.0003% ion present. Other impurities are either present in much smaller quantities or are not significant from the standpoint of sulfite oxidation catalysis.

Extreme care was taken during the experimental procedure to keep the chemicals as pure as possible. Weighing of chemicals, done on a Mettler or an Ainsworth balance with $\pm$ 0.0001 gm sensitivity, was performed in clean pyrex flasks with the aid of a teflon spatula. All glassware was kept extremely clean at all times with the aid of the cleaning solution and constant rinsing with deionized water. Preparation of Na_2SO_3 solution was done immediately prior to the start of the reaction, so that the solution would not be in contact with either the pyrex preparation flask or the burette for more than a few minutes.

As can be seen in Appendix C, the maximum amount of impurities from the chemicals used gives concentrations of around 3×10^{-9} M copper and 7×10^{-8} M iron. Since it appears that copper is a much better catalyst than iron, it seems that we achieved a satisfactory level of purity for the uncatalyzed reaction.

Results

In order to determine how rapidly oxygen could be transferred to the solution, a series of runs with cobalt catalyst was performed. Cobaltous sulfate is known to be an extremely powerful catalyst for sulfite oxidation and it is obvious that for a solution containing 10^{-4} M $CoSO_4$, the rate of reaction would be so rapid that the process had to be mass-transfer controlled in our system. Our 50-ml. reacting solution contained 1.2×10^{-4} M

$CoSO_4$ and runs were made at an initial pH of 10.5. The rate of mass transfer of oxygen is shown in Fig. 18. When the solution volume was increased to 500 ml., the stirring speed decreased to 500 r.p.m., and the method of continuous sampling used, a rate of oxygen transfer very similar to Ness'[35] was obtained. The improvement in mass transfer in our system is significant (our scale is in second, Ness' is in minutes). The rate of reaction measured by Fuller and Crist[16] is compared with our rate of oxygen transfer to the solution (Fig. 18), and it is clear that, if the actual rate is not too much faster than that of Fuller and Crist, we would not be mass-transfer controlled and would be capable of obtaining pure kinetic data in our system.

It must be mentioned that Fuller and Crist's experiments were done at a pH of 8.2 - 8.8, while we performed two series of experiments - one at a constant pH of 11.1 (the pH did not change noticeably during the 5 minutes in which the reaction was followed) and one at a variable pH (from 10.25 at t = 0 to 8.7 at t = 5 min.). The initial sulfite concentration was 0.0093 M in all runs.

There was a scatter in our data due to the method used. All of the recorded kinetic data for the uncatalyzed reaction at a constant pH of 11.1 are shown in Fig. 19. Table 6 shows the exact concentrations measured at various times from the start of the reaction. When the average values for each reaction time are calculated, Fig. 20 is obtained. The standard deviation for each data point is also shown. Our results can be compared with the curve that would result from Fuller and Crist's reaction rate constant. Our data fit the first-order kinetics in sulfite quite well, with the rate constant being $k_1 = 0.0053 \pm 0.0005$ sec^{-1}. This represents an error of about 10%.

The concentrations measured in the runs for which the pH varied from 10.25 at t = 0 to 8.7 at t = 5 min. are shown in Fig. 22. Table 7 summarizes these values.

The results show that the rate was independent of the pH. This is not surprising since sulfite is the only SO_2 species existing in solutions that are as basic as ours.

The deficiencies of our method could be described as follows: there are variations in the exact duration of the reaction due to the method of adding sulfite and the splattering of the reacting solution on the walls of the vessel (although the walls are extremely smooth and there was constant and rapid flow back to the bulk solution); as a result, certain portions of the liquid started reacting before others and some portions were not quenched at exactly the same time as others. Furthermore, impurities often interferred with our experiments. If extreme care was not taken, the results would indicate zero sulfite concentration within 2 or 3 minutes. This happened on quite a few occasions and extreme caution had to be exercised in cleaning and preparing the equipment after the incidents. The whole

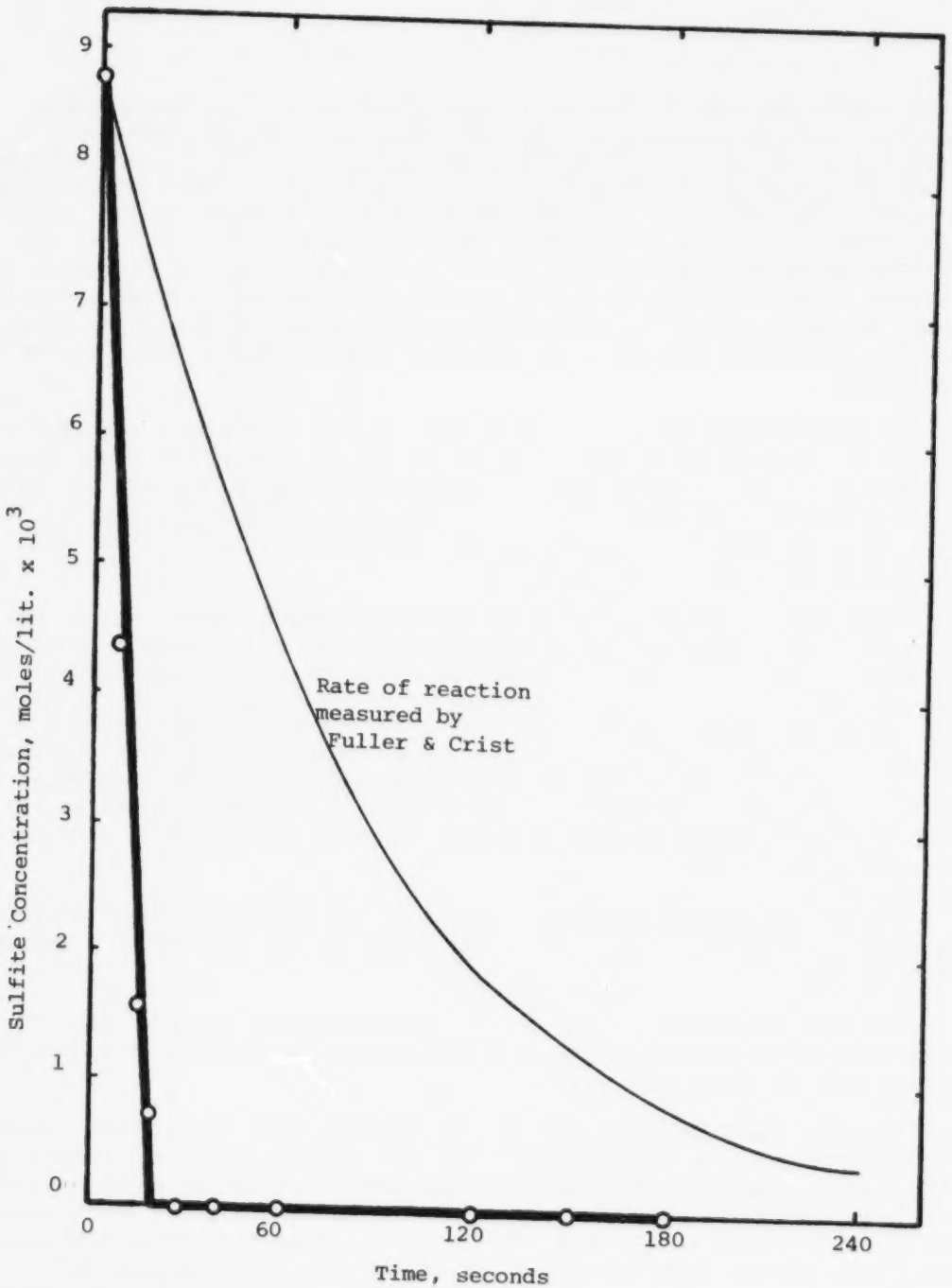


Fig. 18. Rate of mass transfer of oxygen to solution containing 1.2×10^{-4} M $CoSO_4$ catalyst.

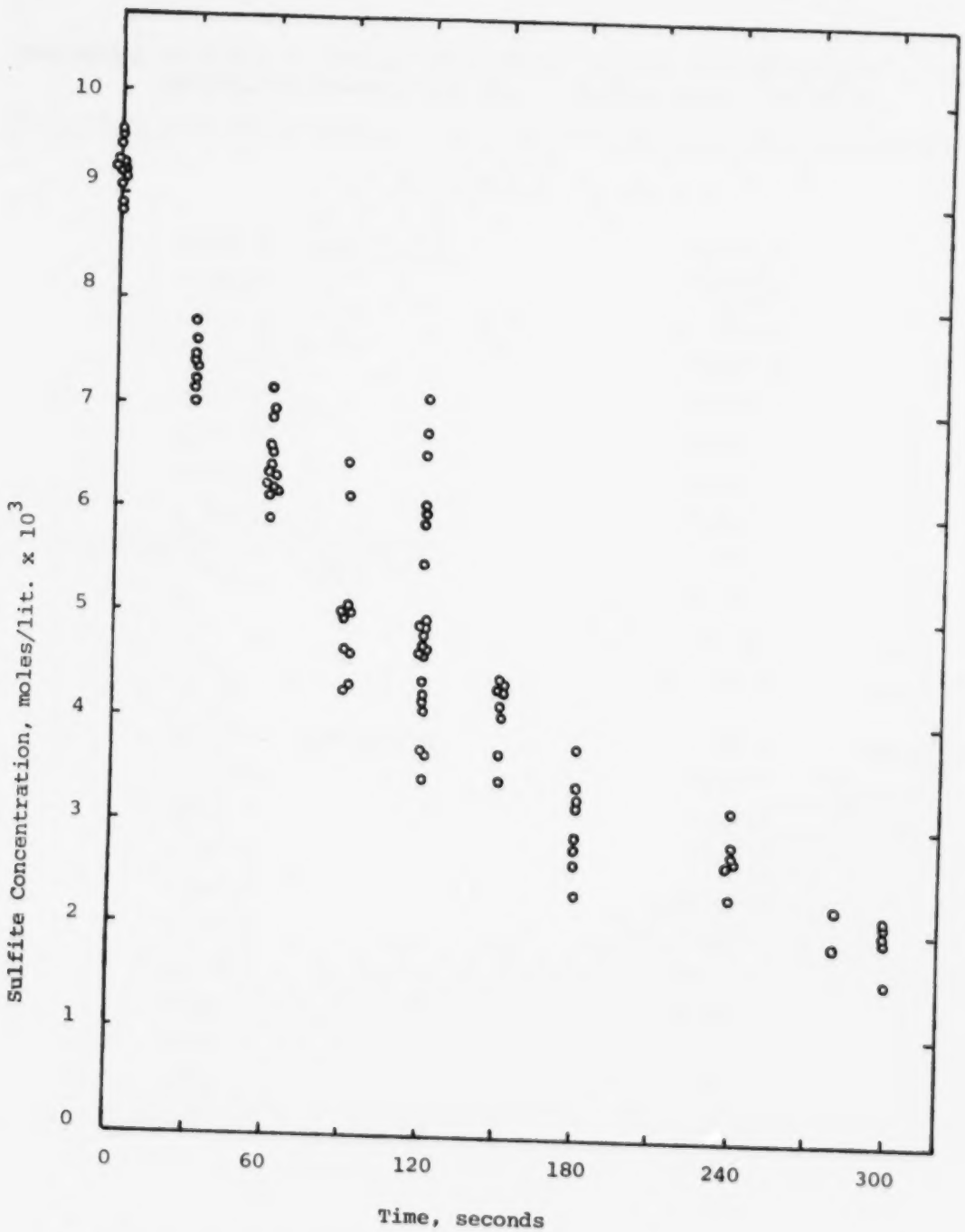


Fig. 19. Complete kinetic data for the uncatalyzed sulfite oxidation at a constant pH of 11.1.

TABLE 6. KINETIC RESULTS FOR THE UNCATALYZED SULFITE OXIDATION AT A CONSTANT pH OF 11.1 (WITH AVERAGE VALUES AND STANDARD DEVIATIONS).

	$[SO_3^{=}]$, M		
t = 0	0.00884	t = 30 sec.	0.00721
	0.00887		0.00735
	0.0923		0.00758
	0.00926		0.00777
	0.00959		0.00735
	0.00908		0.00714
	0.00954		0.00700
	0.00947		0.00742
	0.00922	$[SO_3^{=}]_{t=30}$ =	0.00735±0.00025 M
	0.00928		
	0.00925		
$[SO_3^{=}]_{t=0}$ =	0.00924±0.00024 M		
t = 60 sec.	0.00714	t = 90 sec.	0.00506
	0.00589		0.00613
	0.00630		0.00504
	0.0062		0.00500
	0.00613		0.00463
	0.00694		0.00463
	0.00686		0.00428
	0.00655		0.00426
	0.00656		0.00645
	0.00640		0.00506
	0.00631	$[SO_3^{=}]_{t=90}$ =	0.00506±0.0073 M
	0.00620		
	0.00620		
$SO_3^{=}$ t=60 =	0.00640±0.0036 M		

TABLE 6 (continued)

	$[SO_3]$, M		
t = 120 sec.	0.00340	t = 150 sec.	0.00436
	0.00366		0.00367
	0.00623		0.00413
	0.00492		0.00409
	0.00479		0.00429
	0.00467		0.00340
	0.00485		0.00425
	0.00708		0.00436
	0.00652	$\overline{[SO_3^=]}_{t=150}$	= 0.00404±0.00035 M
	0.00603		
	0.00595		
	0.00408		
	0.00436	t = 180 sec.	0.00232
	0.00588		0.00276
	0.00546		0.00289
	0.00486		0.00324
	0.00428		0.00338
	0.00463		0.00262
	0.00470		0.00317
	0.00422		0.00373
	0.00463	$\overline{[SO_3^=]}_{t=180}$	= 0.00300±0.00045 M
	0.00366		
$\overline{[SO_3^=]}_{t=120}$	= 0.00498±0.00102 M	t = 120 sec.	0.00221
			0.00189
t = 240 sec.	0.00316	t = 300 sec.	0.00152
	0.00264		0.00190
	0.00233		0.00199
	0.00268		0.00205
	0.00282		0.00209
	0.00274	$\overline{[SO_3^=]}_{t=300}$	= 0.00191±0.00023 M
$\overline{[SO_3^=]}_{t=240}$	= 0.00273±0.00027 M		

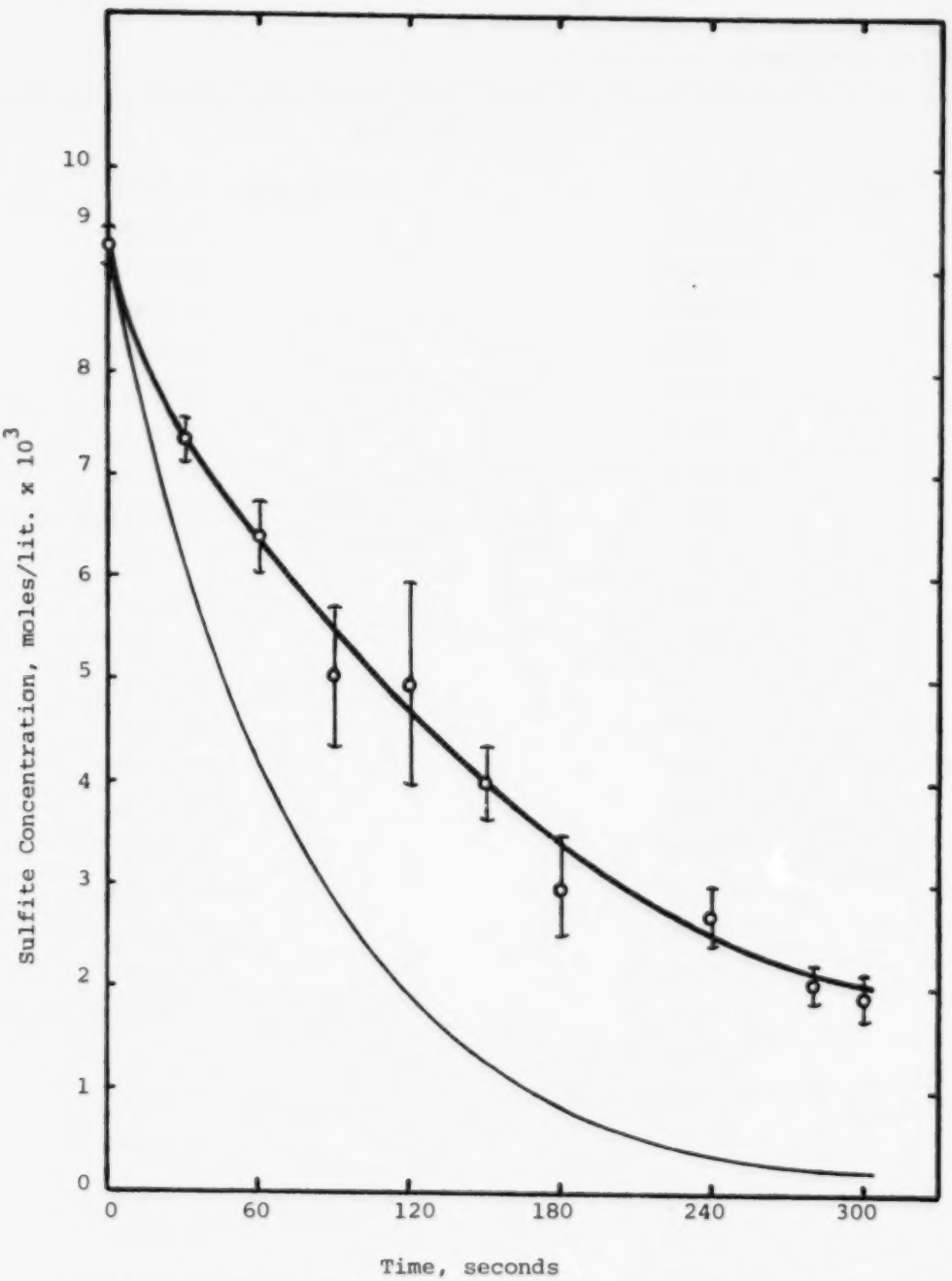


Fig. 20. Average kinetic data and standard deviations for the uncatalyzed reaction at a constant pH of 11.1.

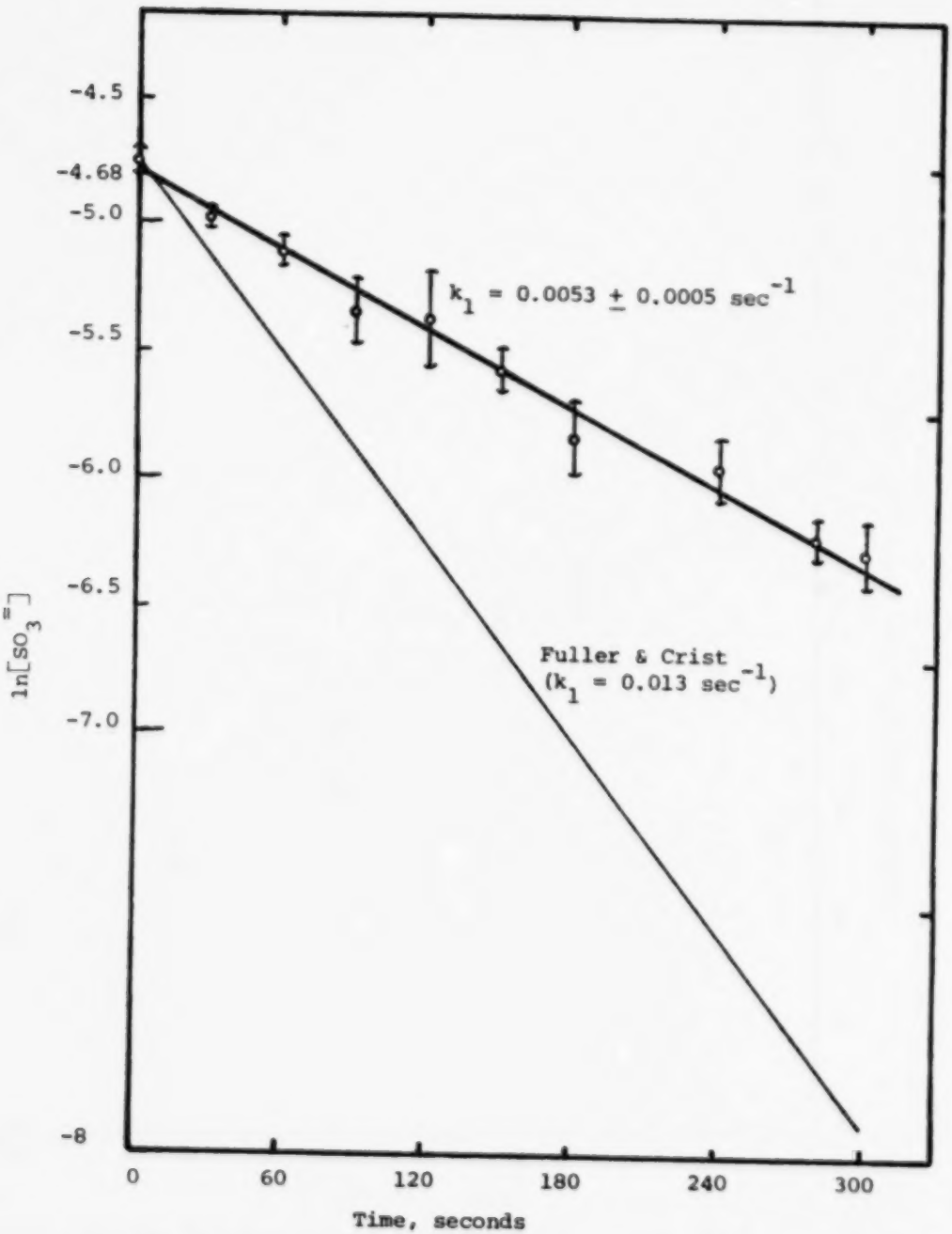


Fig. 21. Natural logarithm of sulfite concentration as a function of time for the uncatalyzed reaction at a constant pH of 11.1.

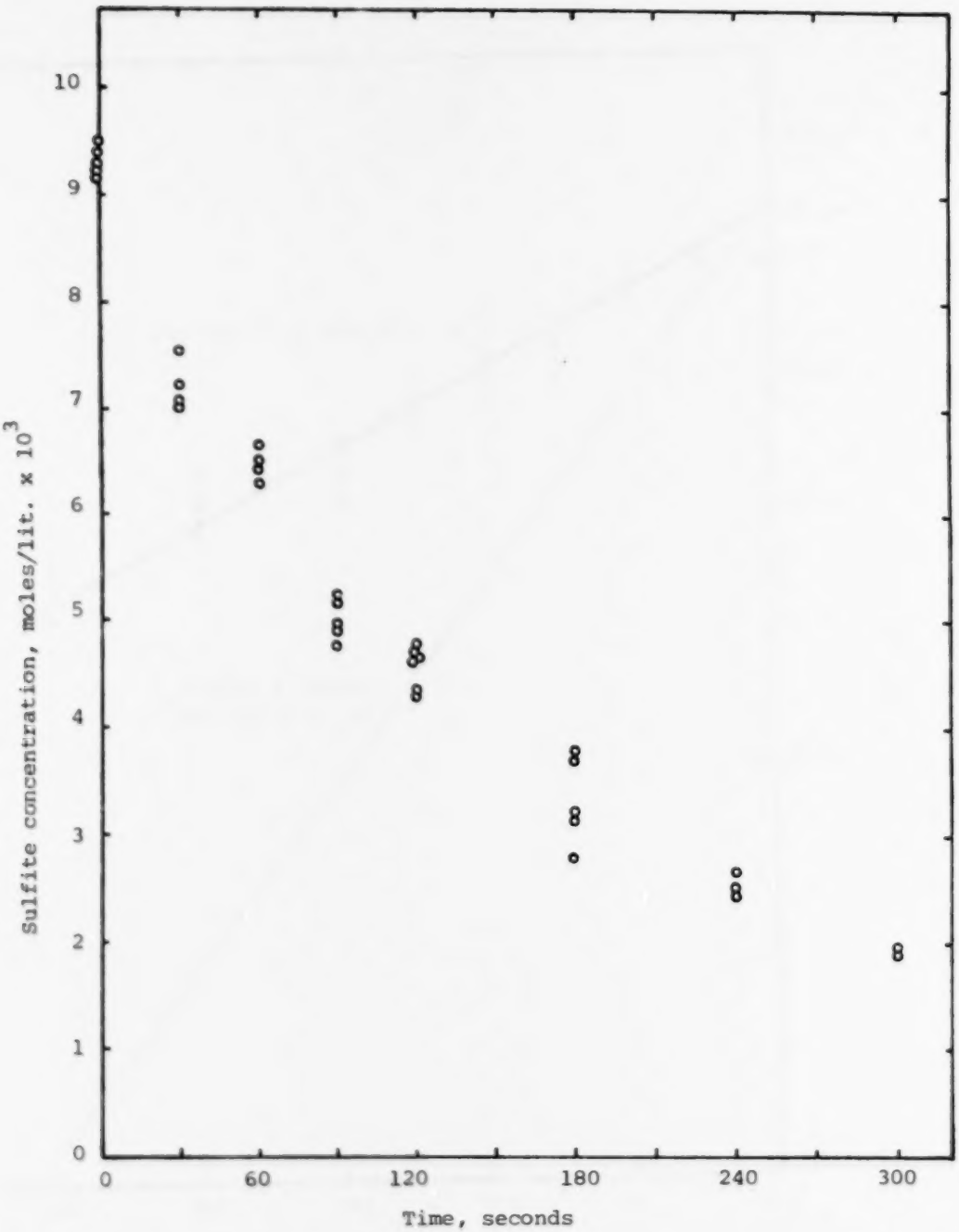


Fig. 22. Complete kinetic data for the uncatalyzed sulfite oxidation at variable pH.

TABLE 7. KINETIC RESULTS FOR THE UNCATALYZED SULFITE OXIDATION AT VARIABLE pH

	$[SO_3^{=}]$, M		
t = 0 (pH=10.25)	0.00927	t = 30 sec.	0.00723
	0.00922		0.00758
	0.00952		0.00707
	0.00940		0.00700
	0.00918		
t = 60 sec.	0.00652	t = 90 sec.	0.00515
	0.00630		0.00518
	0.00666		0.00498
	0.00644		0.00493
			0.00477
t = 120 sec.	0.00479	t = 180 sec.	0.00373
	0.00470		0.00379
	0.00472		0.00324
	0.00463		0.00316
	0.00436		0.00282
	0.00433		
t = 240 sec.	0.00253	t = 300 sec. (pH = 8.7)	0.00191
	0.00247		0.00198
	0.00267		

procedure is very time consuming and that is the primary reason that only experiments with the initial $SO_3^=$ concentration of 0.0043 M were performed and that an attempt at finding the activation energy by running the reaction at some lower temperature was not made. A rapid-mixing flow system would probably be more suitable for this rapid reaction.

We have already seen that the oxygen order of the uncatalyzed reaction is practically not known. It if were zero, we would have, from our results:

$$r = -\frac{d(SO_3^=)}{dt} = k_1 (SO_3^=) \qquad (10)$$

$$\text{with } k_1 = 0.0053 \text{ sec}^{-1}$$

However, if it were one, we would obtain

$$r = k_2 (SO_3^=)(O_2) \qquad (11)$$

$$\text{with } k_2 = 4.08 \text{ (gmole/lit)}^{-1}\text{sec}^{-1}$$

(This was calculated assuming an oxygen solubility of 0.0013 M at $P_{O_2} = 1$ atm.[31])

V. UNCATALYZED STUDIES

A comparison of the kinetic results clearly indicates that the low pH Fe(II) and Mn(II) catalyzed reactions proceed by significantly different reaction mechanisms. For the Mn(II) catalyzed reaction no induction period was observed with the initial reaction rate being independent of pH (0.75-4.0), zero order in oxygen concentration (0.00145-0.01 M), zero order in S(IV) concentration (0.002-0.073 M), and second order in catalyst concentration (1.33×10^{-5} -2.98×10^{-4} M). In contrast, induction periods of up to 100 minutes were observed for the Fe(II) catalyzed reaction. Following the induction period the steady-state reaction rate was dependent on the inverse hydrogen ion concentration (pH 0.89-2.2), zero order in oxygen concentration for $[O_2] < 0.01$ M, and first order in oxygen for $[O_2] \geq 0.01$ M, approximately first order in Fe(II) concentration (6×10^{-5} - 1×10^{-2} M), and dependent upon the 0.60 power of the bisulfite ion concentration. Both the Mn(II) and Fe(II) catalyzed reactions exhibited negative salt effects ($z_A z_B$ = -3.75 and -1.26) and positive activation volumes (+7.2 and +9.9 cc/mole) with apparent activation energies of 19.8 and 31.2 kcal/mole, respectively.

Since the oxidation of aqueous S(IV) has deleterious effects on many flue gas desulfurization systems, there is a need for techniques to effectively inhibit the oxidation reaction. Therefore, the effects of chelating agents (EDTA and 1,10-phenanthroline) and phenolic antioxidants (phenol, phloroglucinol, resorcinol, hydroquinone, pyrogallol, and pyrocatechol) were investigated. The results of the chelation studies led to the somewhat astounding conclusion that the widely studied, previously-accepted "uncatalyzed" reactions were, in fact, primarily trace metal catalyzed. These results indicate that it is only the catalyzed reaction which is of importance to industrial wet scrubbers. While both the low pH Mn(II) and Fe(II) catalyzed reactions are inhibited in the presence of phenolic antioxidants the effects are substantially greater on the Mn(II) catalyzed reaction. However, the activity of the Fe(II) catalyst is markedly more inhibited by chelation with EDTA. The extreme susceptibility of the Mn(II) catalyzed reaction to phenolic antioxidants (present in trace quantities in flue gases) has, in fact, severely limited its usefulness as a catalyst in systems requiring complete oxidation to gypsum. However, at the level of phenolic impurities present, the Fe(II) catalyzed reaction would be relatively unaffected.

The high pH Cu(II) catalyzed reaction was markedly inhibited in the presence of chelating agents (ETDA) of phenolic antioxidants. The most effective inhibitors were those compounds capable of complexing the catalyst in addition to terminating free-radical chains. The tremendous inhibiting

effect of pyrocatechol can be attributed to this dual chelation/antioxidant action. A UV-visible spectrophotometric study of the antioxidant inhibited reactions provided further insight into the inhibitor effects.

VI. APPLICATION OF KINETIC DATA ON SULFUR DIOXIDE OXIDATION TO SCRUBBERS

In industrial SO_2 scrubbers, the pH of the scrubbing solution can vary from 4 to 10, depending on the particular SO_2 absorption method used. We have already described the negative effects of the sulfur dioxide oxidation in Section I. It is interesting to see how some of the kinetic data obtained in our experiments, as well as those reported by other researchers, can be applied to scrubbers in order to evaluate SO_2 oxidation effects.

We shall restrict ourselves to cases where the scrubbing solution contains large amounts of bisulfite or sulfite ions (a good example is the concentrated mode of the double alkali process where the concentration of bisulfite and/or sulfite is greater than 0.5 M). To study the kinetic effects in a flow system of this kind, the theory of gas absorption with simultaneous chemical reaction has to be applied. The book Gas-Liquid Reactions by P. V. Danckwerts[11] represents the most complete work in this area, and the criteria which will be used in our analysis of SO_2 oxidation can be found in Chapter 5 of this book, which is entitled "Absorption into Agitated Liquids".

We shall assume that the scrubber is a packed tower in which SO_2 and O_2 are absorbed by a solution of sodium bisulfite or sodium sulfite (however, the analysis which follows could be applied to any kind of absorption tower). Since SO_2 species are present in the liquid in large excess, oxygen is the limiting reagent, and it is of interest to see how fast it can be absorbed into the solution for the oxidation to take place. The film model for absorption will be used, with the gas-side resistance to mass transfer considered negligible (this is a reasonably good assumption for oxygen absorption since the oxygen solubility in water is rather low. The overall resistance to mass transfer consists of the gas-side resistance and the liquid-phase resistance: $1/K_G = 1k_G + H_e/k_L$, where $H_e = P_{O_2}/C_{O_2}$. H_e for oxygen is of the order of 10^6 atm cm^3/mole and the term H_e/k_L is the dominant resistance term since k_G and k_L usually do not differ by more than two or three orders of magnitude)[11]. To see how strong the effect of SO_2 liquid-phase oxidation on the process is, we shall calculate the absorption enhancement factor, which is the ratio of the absorption rate into a reacting liquid to the absorption rate if there were no reaction (physical absorption rate). The enchancement factor is, therefore, the factor by which the rate of absorption is increased by the reaction.

For an irreversible reaction

$$A(gas) + B(liquid) \longrightarrow products \qquad (12)$$

which is m-th order in A and n-th order in B, and whose rate is therefore

$$r = k_{mn}(A)^m(B)^n \qquad (13)$$

the following dimensionless quantity was found to be of extreme importance in determining the enhancement factor and the absorption rate

$$M = \frac{1}{k_L^2} \left[\frac{2}{m+1} \; k_{mn} \; D_A (A^*)^{m-1} \; (B^o)^n \right] \qquad (14)$$

where k_L = mass-transfer coefficient of the liquid film, cm/sec

m = order of reaction with respect to reactant A

k_{mn} = reaction rate constant, whose units depend on orders m and n

D_A = diffusion coefficient of gas A in solution, cm^2/sec

A^* = concentration of dissolved gas corresponding to equilibrium with the partial pressure of the gas at the interface between gas and liquid, $gmole/cm^3$

B^o = bulk concentration of liquid reactant B, $gmole/cm^3$

n = order of reaction with respect to reactant B

In the case of SO_2 liquid-phase oxidation, oxygen is the gas A, while bisulfite or sulfite (depending on the pH considered) is the reactant B.

Let us first consider the case where the pH of the scrubbing solution is around 4. Bisulfite is the species present in solution, and the data obtained in our experiments can be used.

We shall assume that the temperature in the scrubber is 25°C because that is the only temperature for which we have kinetic data. We shall also assume that manganese is present in solution at 3 r.p.m. The partial pressure of oxygen in the gas phase is taken as 0.04 atm. (this value taken from Johnstone and Singh[26] who give typical composition of flue gases from which SO_2 is scrubbed). The order of reaction with respect to both reactants is taken as zero ($m = 0$, $n = 0$). Sodium bisulfite concentration in the scrubbing liquid is 0.5 M. k_L is taken as 10^{-2} cm/sec (a typical value for packed towers taken from Danckwerts[11], p. 214).

Under these conditions, we have the following:

$$A^* = (O_2) = 2.44 \times 10^{-8} \text{ gmole/cm}^3 \text{ (obtained from Reith[42])}$$

$$D_A = D_{O_2} = 1.85 \times 10^{-5} \text{ cm}^2/\text{sec (Reith[42])}$$

$$B^o = (NaHSO_3) = 0.5 \times 10^{-3} \text{ gmole/cm}^3$$

With no sulfate present in the scrubber,

$$j_{mn} = k_o = 10.6 \times 10^{-4} \text{ moles/lit.hr.} = 2.94 \times 10^{-10} \text{ moles/cm}^3\text{sec}$$

(from our experimental data).

The dimensionless quantity M then becomes

$$M = \frac{1}{k_L^2} \left[2 \; k_o \; D_{O_2} \; (O_2)^{-1} \right] = 0.067 \qquad (15)$$

According to Danckwerts'[11] theory of gas absorption with chemical reaction, when M 1, as in this case, the enhancement factor is close to one, which means that the bisulfite oxidation is relatively slow and does not enhance the absorption of oxygen significantly. In scrubbers whose operating conditions are close to the ones described here, the SO_2 liquid-phase oxidation does not appear to represent a problem.

However, most scrubbers operate at higher pH values. As discussed before, the kinetic data for high pH catalyzed SO_2 oxidation are very scarce, especially for good catalysts like manganese and iron, which are most likely to be present in industrial scrubbers. In the following illustrative calculation, we shall use Reith's[42] data for $CoSO_4$ catalyst. The catalyst concentration in the scrubbing solution is taken as 7×10^{-5} M (around 11 p.p.m.). If the relative catalyst efficiency at high pH is anywhere close to that at low pH, then, according to Junge and Ryan[28], 11 p.p.m. $CoSO_4$ would be roughly as efficient as 2 p.p.m. $MnSO_4$. This, however, is only hypothetical; actual kinetic data at high pH are definitely needed.

For the scrubber, we shall assume the following:

pH = 8

temperature = 50°C (temperature typical of many SO_2 scrubbing systems, according to Schmidt[44])

$P_{O_2} = 0.04$ atm.

$A^* = (O_2) = 2.2 \times 10^{-8}$ g mole/cm^3 (Reith[42])

$D_{O_2} = 3.26 \times 10^{-5}$ cm^2/sec (Reith[42])

$k_L = 10^{-2}$ cm.sec (Danckwerts[11])

$B^o = (Na_2SO_3) = 0.8$ M $= 0.8 \times 10^{-3}$ gmole/cm^3

Under these conditions, Reith[42] has found that the reaction is second order in oxygen and zero order in sulfite. For the catalyst concentration of

7×10^{-5} M, he obtained $k_{mn} = k_2 = 4.9 \times 10^9$ cm^3/gmole sec.

The dimensionless quantity M becomes

$$M = \frac{1}{k_L^2} \left[\frac{2}{3} k_2 D_{O_2} (O_2) \right] = 23.62 \qquad (16)$$

$$\sqrt{M} = 4.86$$

For $\sqrt{M} > 3$, the reaction is rapid and most of the dissolved oxygen reacts in the liquid film. The enhancement factor is equal to $\sqrt{M}$, which means that the absorption rate is enhanced almost five times compared to the case of no reaction.

We can conclude that even at p.p.m. concentration, the catalyst effect on SO_2 oxidation at high pH values in scrubbers is very significant. The oxidation to sulfate is rapid and could amount to a significant percent of the total SO_2 absorbed. Obviously, scrubbing at lower pH values is more desirable from the standpoint of SO_2 liquid-phase oxidation, but the SO_2 absorption effectiveness is decreased in more acidic solutions.

In order for the scrubber calculations at high pH values to have more meaning, kinetic experiments of sulfite oxidation with manganese and other catalysts should be performed. It would also be interesting to see what the effect of the sulfate ions on high pH SO_2 oxidation would be. If a retarding effect, similar to the one observed in our experiments at low pH, should result, addition of sulfate and its recirculation with the scrubbing solution would prevent SO_2 oxidation to a certain extent.

VII. FURTHER STUDIES

Our experimental results and their application to scrubber calculations have only touched upon some of the many questions in the area of SO_2 liquid-phase oxidation. As mentioned in the introduction, our work is only an initial part of an overall kinetic and mechanistic study of the oxidation of sulfur dioxide inall pH ranges.

Most of our experimental work involved the low pH catalyzed oxidation of SO_2. We observed certain characteristics of the reaction which were not reported before. However, a great deal of work still remains to be done in this area. The knowledge of the detailed reaction mechanism should lead to better understanding of the SO_2 oxidation kinetics in general and should facilitate the search for ways of reducing the adverse effects of this reaction. We only touched upon some of the possible steps that could be involved in the overall mechanism. Complexing of the manganese catalyst with sulfate and possibly bisulfite might be involved, as well as the formation of Mn species in the +3 oxidation state. Further work should examine the effects of ionic strength (by changing the ionic strength more drastically than we did, an idea of the species involved in the rate determining step of the reaction could be formed, i.e., whether the species are positive ions, negative ions, or molecules). Determination of the order of reaction with respect to oxygen could bring important clues in investigating the details of the reaction mechanism (in order to vary the oxygen concentration by several orders of magnitude, high pressure kinetic equipment should be used). Spectroscopic studies of possible complexing between various manganese species and sulfate could shed more light on some of the kinetic behavior observed in our experiments. Once a better understanding of the mechanism is achieved, the reasons behind the dimensionless kinetic diagram presented in our work might be found. Since all of our work regarding the various factors affecting the SO_2 catalyzed oxidation rate was done with manganese catalyst, further work should examine other catalysts as well.

In the high pH region, we investigated only the uncatalyzed SO_2 oxidation. The oxygen order and the activation energy of this reaction still remain unknown. The catalyzed reaction, which is of much greater interest, has not been a subject of careful investigation, except for the cobalt-catalyzed case. As a matter of fact, there are almost no data on catalysts which are significant in industrial SO_2 scrubbers and polluted atmospheres. Neither the calculation of oxidation effects in scrubbers nor the modeling of SO_2 oxidation in atmospheric drops to predict sulfate levels in polluted air can be complete without detailed data for the high pH catalyzed reaction. Since

manganese was shown to be the most effective of all catalysts studied at low pH, it seems logical that the first step in further work in the high pH area should include kinetic studies of the manganese-catalyzed reaction. A flow system or an absorption technique would have to be used since the reaction is extremely rapid. Studies of catalysts like iron, copper, magnesium and calcium might also be necessary. With regard to SO_2 oxidation in drops, it would be germane to confirm whether ammonia actually acts as a catalyst or just maintains a pH high enough for sulfite oxidation to take place. It would also be interesting to see whether the addition of sulfate inhibits the high pH oxidation as it did the low pH reaction. As in the low pH case, the prediction or knowledge of the reaction mechanism, which would surely differ from the one at low pH, would be of great practical importance (for example, for the effective inhibition of undesired oxidation effects in scrubbers).

When the overall kinetic study of SO_2 catalyzed reaction in both the low and the high pH regions is complete, optimal operating conditions for scrubbers and various ways of eliminating the adverse effects of SO_2 oxidation in both the scrubbers and the drops should be within reach of realization.

REFERENCES

1. Amdur, M. O., J. Air Pollut. Control Ass., 19, 638 (1969).

2. Astarita, G., Marucci, G., and Coleti, L., Chim. e L'Ind., 46, 1021 (1964).

3. Bäckstrom, J. Amer. Chem. Soc., 49, 1460 (1927).

4. Barron, C. H. and O'Hern, H. A., Chem. Eng. Sci., 21, 397 (1966).

5. Bassett, H., and Parker, W. G., J. Chem. Soc., 1540 (1951).

6. Beilke, S., and Georgii, H. W., Tellus, 20, 435 (1968).

7. Chen, T. I., and Barron, C. H., Ind. Eng. Chem. Fund., 11, 466 (1972).

8. Cheng, R. T., Corn, M., and Frohliger, J. O., Atmospheric Environment, 5, 987 (1971).

9. Coughanowr, D. R., Ph. D. Thesis, University of Illinois, 1956.

10. Coughanowr, D. R., and Krause, F. E., Ind. Eng. Chem. Fundam., 4, 61 (1965).

11. Danckwerts, P. V., Gas-Liquid Reactions, McGraw-Hill, New York, 1970.

12. Davidson, B., J. Air Pollut. Control Ass., 17, 154 (1967).

13. Eriksson, E., Tellus, 4, 215 (1952).

14. Foster, P. M., Atmospheric Environment, 3, 157 (1969).

15. Frydaman, G. N., Torsten, R., and Sillen, L. G., Acta Chem. Scand., 12, 878 (1958).

16. Fuller, B. C. and Crist, R. H., J. Amer. Chem. Soc., 63, 1644 (1941).

17. Gartrell, F. E., Thomas. F. W., and Carpenter, S. B., Am. Ind. Hyg. Ass. J., 24, 113 (1963).

18. Gerhard, E. R., and Johnstone, H. F., Ind. Eng. Chem., 47, 972 (1955).

19. Grozdovskii, Chem. Abst., 2090 (1936).

20. Gunn, D. J., and Saleem, A., Trans. Instn. Chem. Engrs., 48, T46 (1970).

21. Hartridge, H., and Roughton, F. J., Proc. R. Soc., A104, 376 (1923).

22. Hoather, R. C., and Goodeve, C. F., Trans. Farad. Soc., 30, 1149 (1934).

23. Houghton, H., J. Met., 12, 355 (1955).

24. Johnstone, H. F., and Coughanowr, D. R., Ind. Eng. Chem., 50, 1169 (1958).

25. Johnstone, H. G., and Moll, A. J., Ind. Eng. Chem., 52, 861 (1960.

26. Johnstone, H. F., and Singh, A. D., "The Recovery of Sulfur Dioxide from Dilute Waste Gases by Chemical Regeneration of the Absorbent," University of Illinois Bulletin, Vol. XXXVIII, No. 19 (1940).

27. Junge, C. E., Tellus, 8, 127 (1956).

28. Junge, C. E., and Ryan, T. G., Quart. J. Roy. Meteorol. Soc., 84, 46 (1958).

29. Kashtanov andRuizthov, Chem. Abst., 3596 (1956).

30. Laidler, K. J., Chemical Kinetics, Second Edition, McGraw-Hill, New York, 1965.

31. Linek, V. and Mayrhoferova, J., Chem. Eng. Sci., 25, 787 (1970).

32. Matteson, M. J., Stöber, W., and Luther, H., Ind. Eng. Chem. Fund., 8, 677 (1969).

33. McKay, H. A., Atmospheric Environment, 5, 7 (1971).

34. Miller, J. M. and DePena, R. G., J. Geophys. Res., 77, 5905 (1972).

35. Ness, A. I., M. S. Thesis, University of Illinois, 1974.

36. Oddie, B. C., Quart. J. Roy. Meteorol. Soc., 31, 525 (1962).

37. Perry, J. H., Chemical Engineers' Handbook, Fourth Edition, McGraw-Hill, New York, 1963.

38. Petrenchuk, O. P., and Drozdova, V. M., Tellus, 18, 280 (1966).

39. Powell, R. H., M. S. Thesis, University of Illinois, 1973.

40. Pritchett, P. W., Ph. D. Thesis, University of Delaware, 1961.

REFERENCES (continued)

41. Reinders, W., and Vles, S. T., Rec. Trav. Chim., 44, 244 (1925).

42. Reith, T., "Physical Aspects of Bubble Dispersions in Liquids," Thesis, Delft Technical University, Delftsche Uitgevers Maatschappij N.V., 1968.

43. Reith, T., and Beek, W. J., Chem. Eng. Sci., 28, 1331 (1973).

44. Scmidt, M., World Health Organization Project No. U. S. 3100, 1970.

45. Scott, W. D., and Hobbs, P. V., J. Atmos. Sci., 24, 54 (1967).

46. Skoog, A. D., and West, D. M., Fundamentals of Analytical Chemistry, Second Edition, Chapter 20, Holt, Rinehart and Winston, New York, 1969.

47. Srivastava, R. D., McMillan, A. F., and Harris, I. J., Canad. J. Chem. Eng., 46, 181 (1968).

48. Tartar, H. V., and Garretson, H. H., J. Amer. Chem. Soc., 48, 1543 (1926).

49. Titoff, A., Z. Phys. Chem., 45, 641 (1903).

50. Van Den Heuvel, A. P., and Mason, B. J., Quart. J. Roy. Meteorol. Soc., 89, 271 (1963).

51. Vasilev, S. S., Kastanov, L. I., and Kastorkaja, T. L., Acta Physicochim. URSS, 3, 413 (1935).

52. Walter, P. E., M. S. Thesis, University of Illinois, 1972.

53. Wang, J. C. and Himmelblau, D. M., J. Amer. Inst. Chem. Eng., 10, 574 (1964).

54. Westerterp, K. R., Van Dierendonk, L. L., and De Kraa, J. A., Chem. Eng. Sci., 18, 157 (1963).

55. Winkelmann, V. D., Z. Elektrochem., 59, 891 (1955).

56. Yagi. S., and Inoue, H., Chem. Eng. Sci., 17, 411 (1962).

57. Yui, T., Tokyo Inst. Phys. Chem. Res. Bull., 19, 1229 (1940).

APPENDIX A

Sample Calculation of Total Sulfur Dioxide Concentration

- Iodine concentration: 0.01103 N
- Arsenious acid concentration: 0.1012 N
- 5-ml. sample of reacting solution placed in flask containing 10 ml. of iodine and some sodium bicarbonate buffer
- 0.570 ml. of arsenious acid used up in titration

$$(SO_2) = \frac{(10)(0.01103) - (0.570)(0.1012)}{5} = 0.01092 \text{ N}$$

$$= 0.01092 \text{ M}$$

APPENDIX B

Sample Calculation of Sulfite Concentration

- Iodine concentration: 0.0966 N
- Arsenious acid concentration: 0.0996 N
- 0.0650 g of Na_2SO_3 dissolved in 10 ml. of H_2O and added at t = 0 through burette to the oxygenated volume of 40 ml. in the reactor
- After 90 sec., reaction quenched with 15 ml. of iodine; 5 ml. of H_2O used for washing iodine remaining in burette
- 10-ml. sample of quenched solution used for titration
- 1.36 ml. of arsenious acid used up in titration

40 ml. H_2O + NaOH

+ 0.065 g Ha_2SO_3 in 10 ml H_2O

Reacting volume = 50 ml.

+ 15 ml. iodine

+ 5 ml. H_2O

Quenched volume = 70 ml.

Iodine concentration in quenched volume $= \frac{(15)(0.0966)}{70}$

$= 0.02077$ N

Sulfite concentration in quenched volume

$$= \frac{(0.02077)(10) - (1.36)(0.0996)}{10} \text{ N}$$

APPENDIX B (continued)

Sulfite concentration in reacting volume just before quenching

$$= \frac{70}{50} \quad \frac{(0.02077)(10) - (1.36)(0.0996)}{10} = 0.01012 \text{ N}$$

$$= 0.00506 \text{ M}$$

APPENDIX C

Estimated Maximum Concentration of Important Metal Ions Stemming from Chemicals Used

From Na_2SO_3

$$0.0003\% = \frac{3 \times 10^{-6} \text{ g Fe}}{1 \text{ g } Na_2SO_3}$$

$$(Fe)_{max} = \frac{0.0650 \text{ g } Na_2SO_3}{0.05 \text{ lit. reacting solution}} \times \frac{3 \times 10^{-6} \text{ g Fe}}{1 \text{ g } Na_2SO_3}$$

$$\times \frac{1 \text{ mole Fe}}{56 \text{ g Fe}} = 7 \times 10^{-8} \text{ M}$$

From NaOH

$$0.0002\% \text{ iron and copper} = \frac{2 \times 10^{-6} \text{ g}}{1 \text{ g NaOH}}$$

1 N NaOH = 40 g NaOH/lit.

To prepare the initial solution of 40 ml., 0.842 ml. of 1 N NaOH was added to 300 ml. of deionized water.

$$0.842 \text{ ml.} \times \frac{40 \text{ g}}{1000 \text{ ml.}} = 0.03368 \text{ g}$$

$$\frac{0.03368 \text{ g}}{300 \text{ ml.}} = 0.1123 \text{ g NaOH/lit.}$$

$$0.04 \text{ lit.} \times \frac{0.1123 \text{ g NaOH}}{\text{lit.}} = 4.49 \times 10^{-3} \text{ g NaOH in initial 40 ml. solution}$$

In reacting 50 ml. solution:

$$\frac{4.49 \times 10^{-3} \text{ g NaOH}}{0.05 \text{ lit.}} = 0.0898 \frac{\text{g NaOH}}{\text{lit. reacting solution}}$$

APPENDIX C (continued)

$$(Cu)_{max} = 0.0898 \text{ g NaOH} \times 2 \times 10^{-6} \frac{\text{g Cu}}{\text{g NaOH}} \times \frac{1 \text{ mole}}{63.5 \text{ g Cu}}$$

$$(Cu)_{max} = 2.83 \times 10^{-9} \text{ M}$$

$$(Fe)_{max} = 0.0898 \times 2 \times 10^{-6} \times \frac{1}{56} = 3.21 \times 10^{-9} \text{ M}$$

Total

$$(Fe)_{max} = 7.32 \times 10^{-8} \text{ M}$$

$$(Cu)_{max} = 2.83 \times 10^{-9} \text{ M}$$